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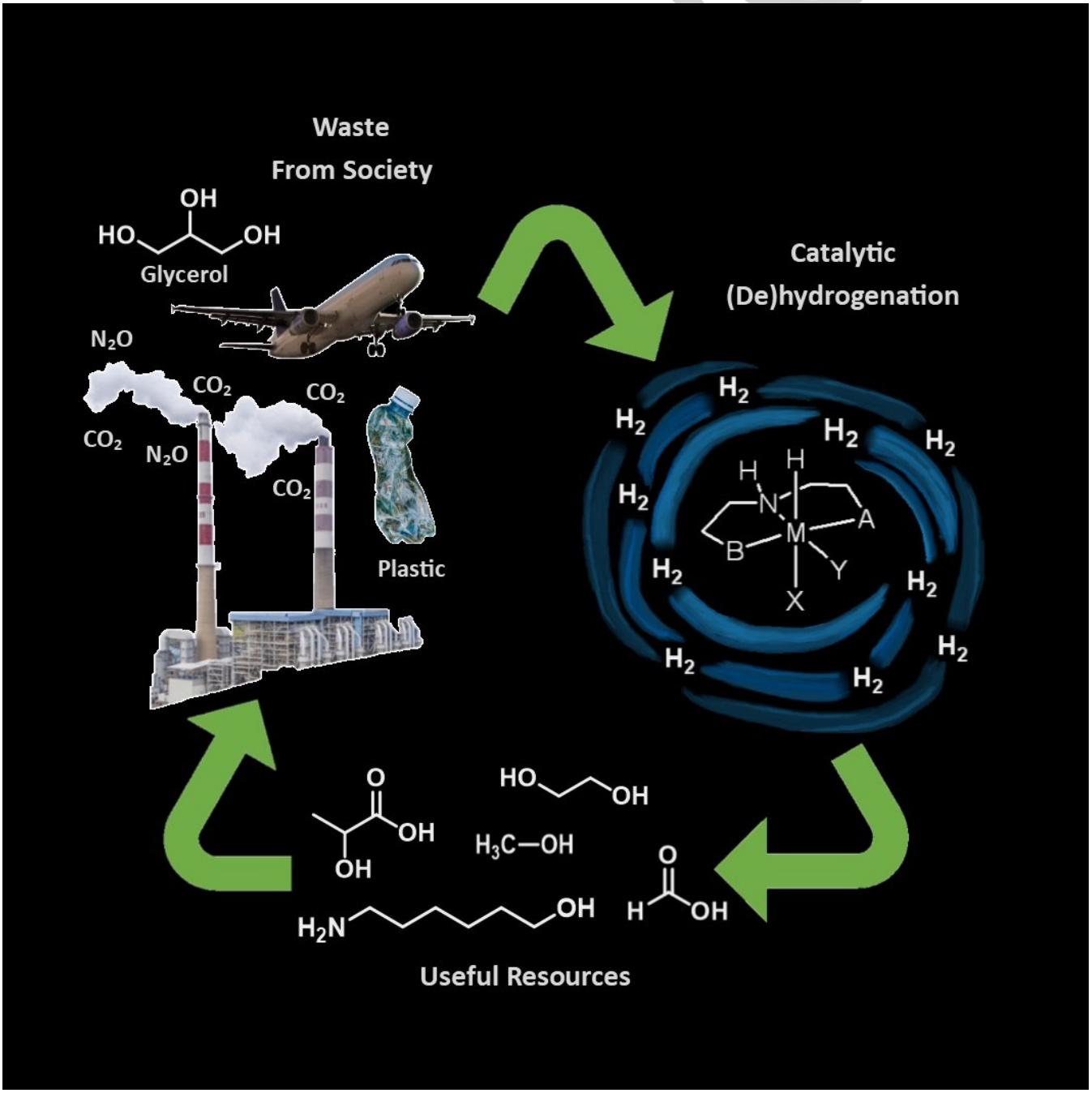
REVIEW

Homogeneous (De)hydrogenative Catalysis for Circular Chemistry – Using Waste as a Resource

Amit Kumar*, Chang Gao



Abstract: Increasing production and usage of several consumer products and energy sources have resulted in the accumulation of substantial amount of waste products that are toxic and/or difficult to biodegrade, thus creating a severe threat to our planet. With the recently advocated concepts of circular chemistry, an attractive approach to tackle the challenge of chemical waste reduction is to utilize these waste products as feedstocks for the production of useful chemicals. Catalytic (de)hydrogenation is an atom-economic, green and sustainable approach in organic synthesis, and several new environmentally benign transformations have been reported using this strategy in the past decade, especially using well-defined transition metal complexes as catalysts. These discoveries have demonstrated the impact and untapped potential of homogeneous (de)hydrogenative catalysis for the purpose of converting chemical wastes into useful resources. Four types of chemical waste that have been (extensively) studied in recent years for their chemical transformations using homogeneous catalytic (de)hydrogenation are CO_2, N_2O, plastics, and glycerol. This review article highlights how these chemical wastes can be converted to useful feedstocks using (de)hydrogenative catalysis mediated by well-defined transition metal complexes and summarizes various types of homogeneous catalysts discovered for this purpose in recent years. Moreover, with examples of hydrogenative depolymerisation of plastic waste and the production of virgin plastic via dehydrogenative pathways, we emphasize the potential applications of (de)hydrogenation reactions to facilitate closed-loop production cycles enabling a circular economy.

1. Introduction

A vast majority of the current chemical production industry is based on a linear economic model of take-make-dispose. This model results in a deficit of important resources, and huge amounts of accumulated waste, which threatens our biosphere. Economists, policymakers, and scientists have thus advocated the concept of a circular economic model based on make-use-reuse-recycle to keep material at its highest utility and value at all times. Chemistry lies at the centre of the production of food, energy, materials, and pharmaceuticals, and thus is crucial to the movement from linear to a circular economic model. Recently, Slootweg has proposed twelve principles of circular chemistry to optimize resource efficiency across chemical value chains.[1] Perspectives on the utilization of innovative green chemical strategies for circular chemistry have also been reviewed recently.[2–5] A fundamental aspect of circular chemistry is to treat waste as a resource to enable a closed-loop production cycle. This specific aim of circular chemistry is the focus of this review.

Reactions based on (de)hydrogenative catalysis are green and sustainable routes for organic synthesis because (a) they are atom-economic, (b) they do not produce any stoichiometric waste as compared to conventional reductants or oxidants, and (c) H_2 can be produced from renewable sources such as by electrolysis of water using electricity produced from solar or wind energy.[6,7] Moreover, chemical production methods based on (de)hydrogenative catalysis offer a strategic theoretical pathway where products can be converted back to the starting materials with the release or chemical capture of hydrogen gas. This unique trait has been exploited for the development of several Liquid Organic Hydrogen Carriers (LOHCs) where hydrogen gas can be produced from the catalytic dehydrogenation of a charged fuel, which later can be regenerated by hydrogenation of the spent fuel.[8,9] The ability to perform the (de)hydrogenation reactions in both directions offers an opportunity to design our production route using (de)hydrogenation process so that the products, which become wastes after use, can be converted back to the starting materials using the reverse reaction. And in doing so, the hydrogen gas produced at the dehydrogenation step can also be recycled for the hydrogenation step (Figure 1).

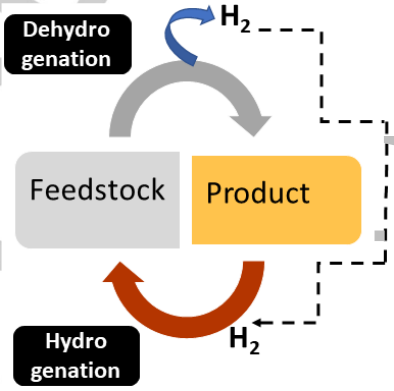


Figure 1. Closed-loop cycle using (de)hydrogenation pathways.

In the previous two decades, several new green organic transformations based on catalytic (de)hydrogenation reactions have been reported. Given the substantial amount of research output, this area has been well-reviewed in recent years from the perspective of both homogeneous[10–12] and heterogeneous catalysts.[13–15] Despite the challenge of catalyst separation associated with homogeneous catalysis that limits its industrial applications, the area of homogeneous catalysis, in contrary to heterogeneous catalysis, allows deeper mechanistic studies strengthening the fundamental understanding of catalyst design and catalytic cycle. Because of this, several new green and sustainable catalytic processes have been developed using homogeneous catalysts. A recent surge of research output has emerged from the catalysis community in the direction of homogeneous (de)hydrogenative catalysis enabled by earth-abundant metals.[16] This direction has enhanced the potential of well-defined molecular complexes towards practical applications.

Our interests lie in both homogeneous catalysis and circular chemistry; in this article, we review the impact that well-defined molecular catalysts have made in recent years to enable closed-loop production cycles using the approach of catalytic (de)hydrogenation. The review focuses on recent advances in catalytic methods to convert waste into useful resources. From the perspective of the impact of the homogeneous (de)hydrogenative catalysis, we have identified four chemicals/materials that have been considered as wastes, either because of their higher supply compared to the demand or because they are harmful to our ecosphere/planet or both. These are CO_2, N_2O, plastics, and glycerol.

Here, we review the (de)hydrogenative catalytic transformation of these four wastes to useful chemical feedstocks

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using well-defined molecular complexes. Summaries of various homogeneous catalysts developed for the transformation of each substrate, along with their limitations and future prospects have been discussed. Considering the substantial research outputs on this topic, comprehensive inclusion of other aspects of catalysis such as heterogeneous catalysis, electrocatalysis, and photocatalysis is beyond the scope of this review.

2. Carbon dioxide

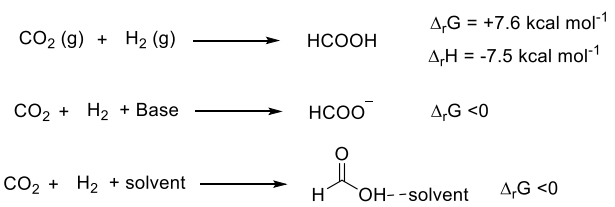
Carbon dioxide is the final product formed upon the burning of fossil fuels (coal, natural gas, and oil) and organic waste. Growing industrial production and our dependence on fossil fuels have increased the production of CO_2 over time. For example, in 2019, 33 gigatons (Gt) of CO_2 were produced globally from the energy sector alone.[17] The ever-rising atmospheric concentration of CO_2 is held responsible for climate change giving rise to problems of global warming and ocean acidification. Converting CO_2 to useful chemicals and fuels presents an attractive opportunity to reduce accumulating waste as well as to lower our dependence on fossil fuels. Several chemicals such as urea, salicylic acid, and polyols are produced industrially using CO_2. However, there is a considerable gap in the amount of CO_2 produced and that consumed. Thus, there is an urgent need to develop efficient technologies to capture and sequester or valorise CO_2. Indeed, there has been an appreciable effort in the area of reactivity of CO_2 with various organic compounds such as alkenes, alkynes, arenes, epoxides, alcohols, amines, boranes, and silanes. [18–25] In the interest of this review as discussed above, here, we summarize recent results in CO_2 valorisation enabled by catalytic hydrogenation pathways using molecular hydrogen. A few other review articles have also been written on the topic of CO_2 hydrogenation using homogeneous catalysts in past years.[26–29]

2.1 Hydrogenation of CO_2 to formic acid

Formic acid (FA) is an important chemical feedstock and has a global demand of around 800, 000 tonnes, with substantial applications in textile, food, and agrochemical industries.[30] It can also be used as a fuel in the FA fuel cell to produce energy. Recently, FA is being advocated as a potential Liquid Organic Hydrogen Carrier (LOHC) for use in a future hydrogen economy.[31,32] Thus, the production of FA from waste CO_2 is an attractive process from the perspective of the circular economy.

Hydrogenation of CO_2 to formic acid or a formate salt was first accomplished using a heterogeneous catalyst in 1914[33] and several heterogeneous catalysts have been studied since then. These catalysts can be divided into three parts: (a) unsupported bulk (e.g. Pd Black and Raney Ni) or nanometal (e.g. Ru or Pd nanoparticles) catalysts, (b) supported bulk or nanometal catalysts (e.g. Pd/Act. carbon, Pd/graphite, Au/Al_2O_3, and Au/TiO_2), and (c) heterogenized molecular catalysts immobilized on grafted solids or porous polymers. In general, the supported metal catalysts showed superior catalytic activity compared to the unsupported ones. The details on the catalytic conditions and outcome of heterogeneous catalysts for hydrogenation of CO_2 to HCOOH or a formate salt have been reviewed recently.[34,35] Although heterogeneous metal catalysts allowed easy separation and recycling of catalysts, the catalytic activity remains poor in most cases. For example, the maximum TOF obtained using supported or unsupported metal catalyst was found to be 836 h^{-1} using Pd/Act. carbon. Since these catalysts involve precious metals, a high activity or the use of earth-abundant metals is desirable for economic viability. In comparison to the heterogeneous catalysts, the number of reports on homogeneous catalytic systems involving both precious and earth-abundant metals is significantly higher. Homogeneous catalysts have also demonstrated much higher catalytic activities such as TONs up to 3 500 000[36], and TOFs up to 1 100 000 h^{-1},[37] compared to any heterogeneous catalyst and is the focus of the review in the following section.

Thermodynamically, direct hydrogenation of CO_2 to HCOOH is an endergonic process (Scheme 1, Δ_rG = +7.6 kcal mol^{-1}).[38] Therefore, most of the catalytic processes use a stoichiometric amount of base to drive the reaction forward by producing the more stable formate salt.[39–42] Despite highly active and selective catalysts developed for the hydrogenation of CO_2 to formate salt (such as one by Nozaki with TOF 150 000 h^{-1} at 200 °C, 50 bar and TON 3 500 000 at 120 °C),[36] use of (i) stoichiometric base and then (ii) stoichiometric acid to produce HCOOH from formate produces significant salt waste, which presents a challenge in the commercialization of this technology.



Scheme 1. Thermodynamics of hydrogenation of CO_2 to HCOOH.

To achieve a circular economy that advocates for the elimination of waste, it is important to develop catalytic processes for the hydrogenation of CO_2 to HCOOH without using a stoichiometric amount of additive. An early example for the hydrogenation of CO_2 to free HCOOH dates back to 1990 using $[Rh(NBD)(PMe_2Ph)_3]BF_4$ complex albeit with a lower TON of 10-60/day.[43] With the new catalyst design, it has been possible to perform hydrogenation of CO_2 to HCOOH under acidic conditions. In 2004, Fukuzumi and Ogo reported the first example of hydrogenation of CO_2 under acidic conditions without using any stoichiometric additive. A water-soluble ruthenium catalyst $[(\eta^6\text{-}C_6Me_6)Ru^{II}(L)(OH_2)]SO_4$ (L = 2,2'-bipyridine or 4,4'-dimethoxy-2, 2'-bipyridine) was used for the hydrogenation of CO_2 (pH_2/pCO_2 = 5.5/2.5 MPa) in water under acidic conditions (pH = 2.5-5.0) to produce HCOOH.[44] However, the activity of the catalyst was significantly lower than those used under basic conditions, and a TON of up to 50 was obtained in 70 h. Later, Fukuzumi and Ogo in 2006 reported iridium aqua complexes $[Cp^*Ir^{III}(L)(OH_2)]^{2+}$ (Figure 2, **Ir-1**, Cp* = $\eta^5\text{-}C_5Me_5$, L = 2,2′-bipyridine) and ruthenium aqua complexes $[(\eta^6\text{-}C_6Me_6)Ru^{II}(L)(OH_2)]^{2+}$ (**Ru-1**, L = 2,2′-bipyridine, 4,4′-dimethoxy-2,2′-bipyridine) for the hydrogenation of CO_2 to HCOOH under acidic conditions.[45]

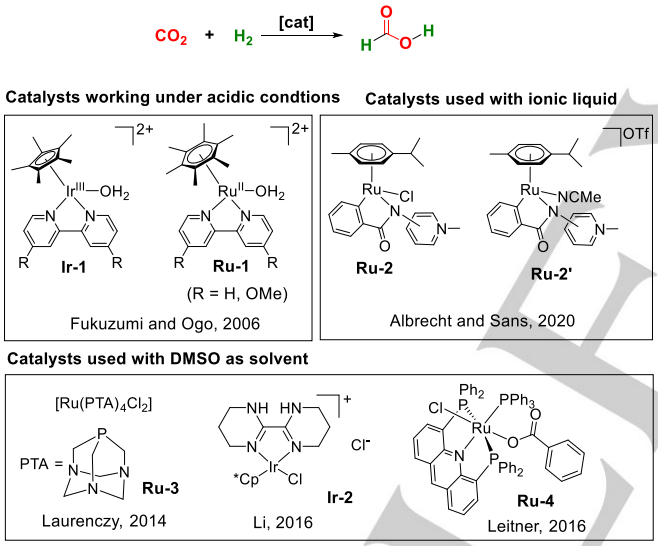


Figure 2. Catalysts for the additive-free hydrogenation of CO_2 to HCOOH.

An approach based on using ionic liquids (ILs) as solvents has also been used for the additive-free hydrogenation of CO_2 to HCOOH.[46] ILs have a high capacity to dissolve CO_2. More importantly, ILs bearing basic anions such as 1,3-propyl-2-methylimidazolium formate (PPMI·O_2CH) can enhance the yield of reaction by thermodynamically stabilizing the product. Sans and Dupont reported hydrogenation of CO_2 to HCOOH using $[Ru_3(CO)_{12}]$ and an imidazolium-based IL associated with the acetate anion.[47] Based on the experimental observations, the authors suggest a dual role of IL: (i) it assists in the formation of catalytically active Ru-H species, and (ii) it acts as an acid buffer driving the reaction equilibrium towards the formation of free HCOOH. A high TON of 17,000 was observed and a good yield (1.2 M) of HCOOH was observed. Ruthenium catalysts (**Ru-2,2'**, Figure 2) based on pyridylidene amide (PYA) ligand have also been utilized to perform hydrogenation of CO_2 to HCOOH recently by Albrecht and Sans. A TON of up to 4,520 was observed in H_2O/DMSO solvent mixture in the presence of an IL.[48]

In the direction of additive-free hydrogenation of CO_2 to HCOOH, the use of polar solvents such as H_2O or DMSO for performing catalysis has also shown promising results. These solvents can stabilize HCOOH by performing hydrogen bonding thus driving the reactions forward (Scheme 1). Laurenczy has reported that using a homogeneous ruthenium catalyst $[RuCl_2(PTA)_4]$ (**Ru-3**, PTA = 1,3,5-triaza-7- phosphaadamantane, Figure 2), CO_2 can be hydrogenated in H_2O or DMSO to form HCOOH without using any additive.[49] 0.2 M HCOOH can be produced in H_2O at 200 bar and 60 °C whereas in DMSO, 1.9 M HCOOH can be obtained. The catalyst was found to be very stable and could be recycled multiple times without loss of activity. Soon after, Li reported an iridium catalyst (**Ir-2**, Figure 2) bearing an N,N'-diimine ligand for the direct hydrogenation of CO_2 to HCOOH without using any additive.[50] A TON of >10,000 was obtained at 40 °C and 76 bar (7.6 MPa) of H_2/CO_2 (1 : 1) in H_2O. Along this line, Leitner reported ruthenium acriphos pincer catalyst (**Ru-4**, Figure 2) for the hydrogenation of CO_2 to HCOOH in H_2O or DMSO solvent that exhibits a TON of up to 4,200 and TOF of up to 260 h^{-1} at 60 °C and 80 bar H_2 and 40 bar CO_2.[51] However, the lower yield of HCOOH (up to 0.33 M) was obtained compared to that of Laurenczy (up to 1.9 M). The lower product yield was attributed to the product-dependent catalyst inhibition and was overcome by the addition of acetate buffer. This resulted in a high concentration of free HCOOH of 1.27 M. DFT calculations support the stabilization of HCOOH by hydrogen bonding from solvents – H_2O or DMSO.

2.2 Hydrogenation of CO_2 to methanol and higher alcohols

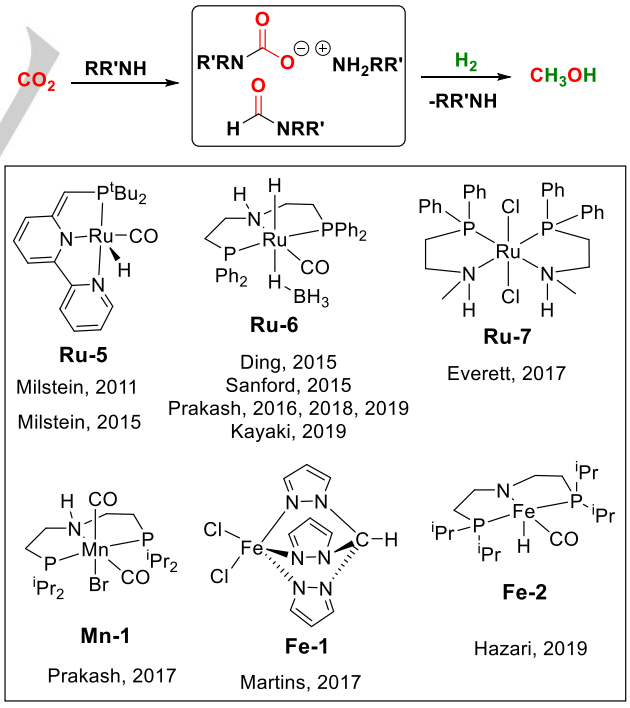


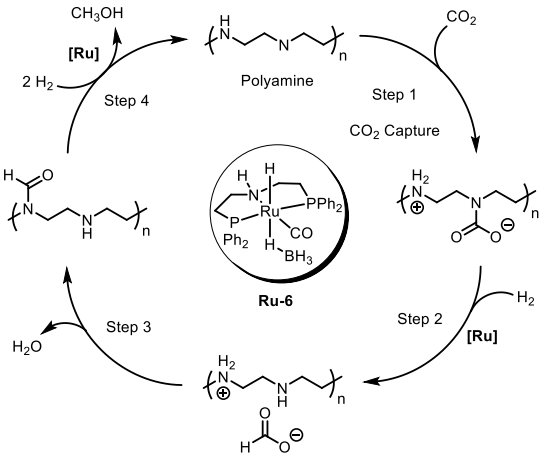
Figure 3. Hydrogenation of CO_2 to CH_3OH using amines.

Methanol, with a global demand of more than 75 million tons annually, is one of the most important feedstocks of chemical industries such as for the production of formaldehyde, acetic acid, methyl *tert*-butyl ether (MTBE), hydrocarbons, and olefins.[52] It

also has several applications in the energy sector, for example, as fuel in internal combustion engines, as energy carriers, and for the production of biodiesel. Thus, the topic of producing methanol from CO_2 is highly attractive and has been intensively studied by the catalysis community. The concept of 'Methanol Economy' for the sustainable production of methanol from CO_2 has been advocated by the Nobel Laureate Prof. George A. Olah and Prof. Surya Prakash.[53] Hydrogenation of CO_2 to methanol is an endothermic process and therefore requires a high temperature. Almost all the catalysts reported to date for the direct and additive-free hydrogenation of CO_2 to methanol are heterogeneous in nature.[35,54–56] Heterogeneous catalysts have also been commercialized for the production of methanol by the hydrogenation of CO_2. For example, $Cu/ZnO/Al_2O_3$ catalyst that operates at 220–300 °C and 5–10 MPa was commercialized by Imperial Chemical Industries in the 1960s. Since then, Cu-ZnO-based materials have attracted substantial attention, and still remain the most investigated type of heterogeneous catalysts for the catalytic hydrogenation of CO_2 to methanol.[57] Cu-ZnO-based catalysts have also been utilized in the Mitsui Process by the RITE and NIRE (Japan), and the Lurgi Process by Lurgi for the conversion of CO_2 to methanol. A few years ago, in 2012, the Carbon Recycling International started the production of 100% renewable methanol from the direct hydrogenation of CO_2 (captured from emission) to methanol where hydrogen gas was produced by the electrolysis of water using renewable electricity. Despite the industrial applications of heterogeneous catalysts, catalysts based on well-defined molecular complexes have demonstrated promising activity for the hydrogenation of CO_2 to methanol especially under relatively milder reaction conditions (e.g. temperature <150 ºC).

Hydrogenation of CO_2 to methanol using homogeneous catalysts have been demonstrated using indirect sequential approaches except for the example discussed in Scheme 3. This sequential concept was first realized by Milstein and co-workers (2011) who reported ruthenium pincer catalysts (e.g. **Ru-5**, Figure 3) for the hydrogenation of formates, organic carbonates, and organic carbamates to methanol.[58] As these species can be readily formed by the reaction of CO_2 with alcohols/amines, their hydrogenation to methanol provides an alternative strategy for the indirect conversion of CO_2 to methanol using molecular hydrogen. Since then, several homogenous catalysts have been utilized for the hydrogenation of CO_2 to methanol in the presence of additives such as amines and alcohols. The first example of the hydrogenation of CO_2 to methanol via cascade catalysis was demonstrated by Sanford.[59] A three-step methodology was used – (i) Hydrogenation of CO_2 to HCOOH in the presence of $(PMe_3)_4Ru(Cl)(OAc)$ (ii) esterification of HCOOH in the presence of $Sc(OTf)_3$ catalyst and (iii) hydrogenation of formed formate ester to methanol in the presence of a RuPNN pincer catalyst (**Ru-5**, Figure 3). Although an overall transformation of CO_2 to methanol was successfully demonstrated, a low TON (up to 21) was observed. Recently, Goldberg has used the same approach and obtained a higher TON (428) using the catalytic combination of $Ru(H)_2[P(CH_2CH_2PPh_2)_3]/Sc(OTf)_3$/Ir-(tBuPCP)(CO).[60] After the seminal works of Milstein and Sanford, several examples have been reported where CO_2 is captured by a nucleophile such as amines and alcohols to form a species whose hydrogenation to methanol is more favourable compared to the direct hydrogenation of CO_2 to methanol.

Hydrogenation of CO_2 to methanol in the presence of amines was first demonstrated by Sanford in 2015 using $NHMe_2$ and a ruthenium-Macho catalyst (**Ru-6**, Figure 3).[61] $NHMe_2$ in the presence of CO_2 (2.5 bar) and H_2 (50 bar) formed dimethylammonium dimethylcarbamate (DMC) and dimethylformamide (DMF) which was subsequently hydrogenated to methanol. The overall process was also demonstrated as a single step where CO_2 (2.5 bar) was hydrogenated (50 bar) to methanol (TON = 550) in the presence of the ruthenium pincer catalyst (**Ru-6**, 0.03 mol%, Figure 3), K_3PO_4 (0.25 mmol) and $NHMe_2$ (7.6 mmol). Around a similar time, Milstein reported the capture of low-pressure CO_2 (1 atm) using amino-ethanol followed by subsequent ruthenium (**Ru-5**, Figure 3) catalysed hydrogenation to form methanol with the release of amino-ethanol.[62] Using this approach, Ding reported hydrogenation of CO_2 to methanol in the presence of morpholine and ruthenium-Macho pincer catalyst (**Ru-6**, Figure 3) in two steps via the formation of N-formylmorpholine.[63] Using a new avenue in this direction, the group of Prakash and Olah demonstrated for the first time in 2016 an integrated process by combining CO_2 capture and hydrogenation.[64] In this approach, CO_2 is first captured from the air (CO_2 concentration 400 ppm) using a scrubbing agent such as polyamines to form mixtures of carbamates and carbonates/bicarbonates and then subsequently hydrogenated using a ruthenium-Macho pincer catalyst (**Ru-6**, Figure 3) to form methanol. A very good yield of CH_3OH (79%) was obtained and recyclability of the catalyst was also demonstrated for up to five times exhibiting a TON > 2000. A proposed mechanism for this transformation has been outlined in Scheme 2. CO_2 is captured by a polyamine to form a carbamate (step 1) which subsequently gets hydrogenated in the presence of the ruthenium pincer catalyst to form a formate salt (step 2). Dehydration of the formate salt results in the formation of a formyl intermediate (step 3) which then is converted to methanol via ruthenium catalysed hydrogenation process (step 4). A more detailed mechanism for the final step i.e. hydrogenation of formamide to methanol using an analogous ruthenium complex has been reported recently by the same group.[65]



Scheme 2. Hydrogenation of CO_2 captured using scrubbing agents to CH_3OH by Prakash and Olah (2016).

Later, Prakash in 2018 employed a biphasic 2-MeTHF/water solvent system that allowed easy separation and

recycling of both amine and catalyst.[66] Utilising this strategy, not only a higher yield of CH_3OH (>90%) was obtained but more efficient recycling of both amines and the catalyst was demonstrated with 95% of the catalyst activity after four cycles. To further enhance the recyclability of amines, in 2019, Prakash employed amines that were immobilized onto a solid support.[67] A highly active ruthenium catalyst (**Ru-7**, TON up to 8900, Figure 3) was reported by Everett and co-workers for the hydrogenation of CO_2 to methanol via formamide in the presence of amines.[68] Prakash has also used a polyamine for the hydrogenation of CO_2 to methanol in the presence of a ruthenium-Macho pincer catalyst (**Ru-6**, Figure 3) exhibiting a TON of up to 9900.[65] Along this line, the use of poly(ethyleneimine) has also been recently reported by Kayaki for the hydrogenation of CO_2 to methanol in the presence of a ruthenium-Macho pincer catalyst (**Ru-6**, Figure 3).[69] For all these above-mentioned systems, the hydrogenation mechanism is proposed to be assisted by metal-ligand cooperation.

Other than ruthenium, some base-metal complexes have also been employed for the amine-assisted hydrogenation of CO_2 to methanol. Prakash reported an air-stable Mn(I)-PNP pincer catalyst (**Mn-1**, Figure 3) for hydrogenation of CO_2 to methanol via the formation of formamide using an amine such as morpholine or benzylamine.[70] Although a high yield of methanol (84% with benzylamine and 71% with morpholine) was obtained, the TON was significantly lower (up to 36) compared to ruthenium systems. More active catalysts in this direction were reported using iron complexes by the groups of Martins (**Fe-1**, Figure 3) and Bernskoetter (**Fe-2**, Figure 3).[66-67]

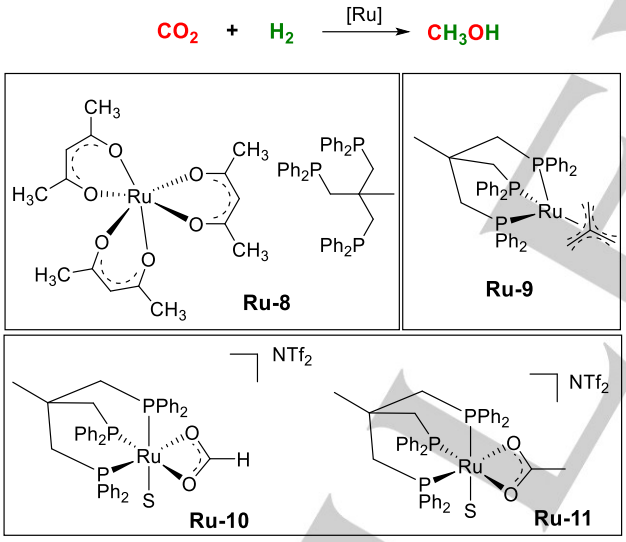
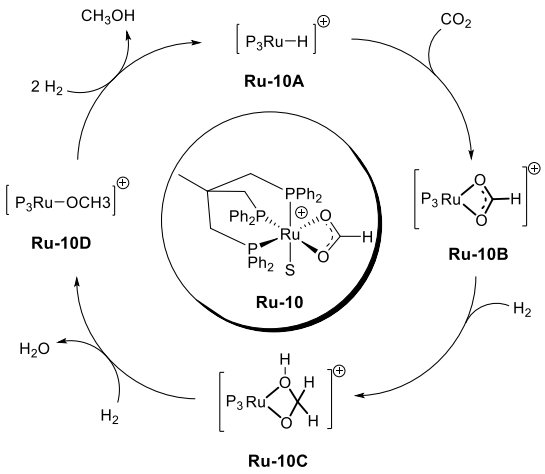


Figure 4. Hydrogenation of CO_2 to CH_3OH in the presence or absence of alcohols.

Other than amines, alcohols have also been utilized for the purpose of CO_2 capture and subsequent hydrogenation to methanol. After Sanford's seminal discovery in 2011[59] of the hydrogenation of CO_2, in 2012, Klankermayer, Leitner, and co-workers demonstrated hydrogenation of CO_2 to methanol using ethanol as an additive.[71] In the presence of ethanol, hydrogenated CO_2 was captured as ethyl formate and subsequently hydrogenated to methanol. A combination of ruthenium(II)-triphos complex and a Lewis acid bis(trifluoromethane)sulfonimide ($HNTf_2$) was used as a catalyst that exhibited a TON of 221. The ruthenium(II)-triphos complex could be generated either *in situ* from $Ru(acac)_3$ and Triphos (**Ru-8**, Figure 4) or from the readily accessible ruthenium(ii)-complex [(Triphos)Ru(TMM)] precursor (**Ru-9**, Figure 4). Recycling of the catalyst was demonstrated in a biphasic system of 2-MeTHF-water and an overall TON of 769 was achieved after 4 cycles. Interesting insights into the mechanism were reported later by experiments and DFT calculations by Klankermayer and Leitner.[72] Experimental studies revealed that the role of co-catalyst $HNTf_2$ is to form the cationic complex **Ru-10** (Figure 4) which was confirmed to be the active species. Based on this insight, an analogous complex [(Triphos)Ru(η^2-OAc)(S)][NTf_2] (**Ru-11**, with S being a free coordination site or weakly bound solvent molecule, Figure 4) was synthesized. Remarkably, complex **Ru-11** or complex **Ru-9** with $HNTf_2$ (1 equivalent) was able to catalyse the hydrogenation of CO_2 to CH_3OH even in the absence of alcohol additive exhibiting a TON up to 348 (140 °C, reaction time 24 h). Recyclability of the catalyst was also demonstrated reaching a TON of 769 after 4 cycles. Notably, this was the first example of the direct hydrogenation of CO_2 to CH_3OH using a homogenous molecular catalyst without needing an additive. A mechanism as outlined in Scheme 3 was proposed on the basis of DFT calculations. Catalysis starts with the ruthenium hydride complex **Ru-10A** that can be generated from the hydrogenation of complex **Ru-10** or **Ru-11**. The insertion of CO_2 to **Ru-10A** results in the formation of the ruthenium-formate complex **Ru-10B** that was also spectroscopically characterised. The reaction of **Ru-10B** with one equivalent of H_2 results in the formation of ruthenium–hydroxymethanolate complex **Ru-10C** which subsequently gets hydrogenated to form ruthenium–methanolate complex **Ru-10D**. The reaction of **Ru-10D** with H_2 eliminates CH_3OH and regenerates the ruthenium hydride complex **Ru-10A**.



Scheme 3. Proposed catalytic cycle for the hydrogenation of CO_2 to methanol using **Ru-10** catalyst. P_3Ru denotes the Triphos–Ru(II) fragment.

Using a similar ligand system, Beller in 2017 reported hydrogenation of CO_2 to methanol in THF/EtOH enabled by a homogeneous catalyst of base-metal formed from the combination of $[Co(acac)_3]$, Triphos, and $HNTf_2$.[73] A TON of 50 was obtained at 100 °C at 20 bar of CO_2 and 70 bar of H_2. Later, Beller reported a higher TON of up to 125 using modified triphos ligands, $[Co(acac)_3]$, and $HNTf_2$.[74] Along a similar direction, Klankermayer in 2019 reported that a combination of Ru-

triphos/Lewis acid can catalyse the transfer hydrogenation of CO_2 to methanol using linear alcohols as the hydrogen donor.[75] Recently, Prakash has reported an integrated CO_2 capture and hydrogenation process using an alkali metal hydroxide and ethylene glycol.[76] CO_2 is captured as a carbonate salt e.g. potassium 2-hydroxyethyl carbonate in the presence of KOH and ethylene glycol and is subsequently hydrogenated to methanol using a ruthenium-Macho pincer catalyst (**Ru-6**, Figure 3) with the liberation of KOH and ethylene glycol. Reviews detailing advantages of methanol economy and different routes for the production of methanol have been reported in past years.[77–79]

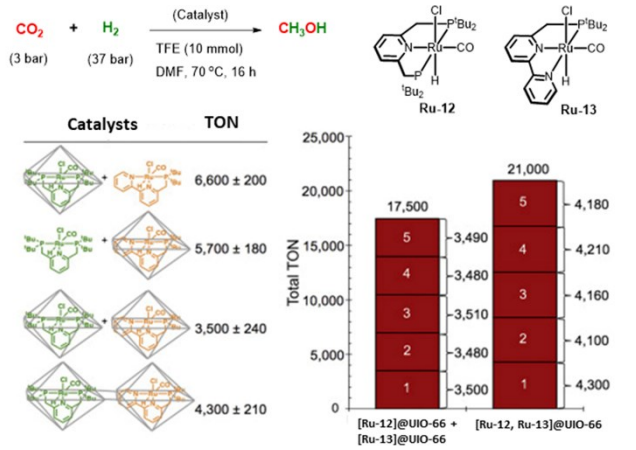


Figure 5. Catalytic activity of MOF encapsulated pincer complexes **Ru-12** and **Ru-13** for hydrogenation of CO_2 to CH_3OH. Reproduced with permission from reference 80. Copyright 2020 Elsevier.

Recently, a bioinspired approach based on a multicomponent catalyst system has been developed by Byers and Tsung for the hydrogenation of CO_2 to methanol.[80] The three-component catalytic system involves – (a) RuPNP pincer complex (**Ru-12**, Figure 5) for the hydrogenation of CO_2 to formic acid, (b) MOF UiO-66, which is Lewis acidic in nature, for the esterification of formic acid to form a formate ester, and (c) Milstein's RuPNN pincer catalyst **Ru-13** (Figure 5) for the hydrogenation of the formate ester to methanol. The separation of three catalysts to avoid poisoning was achieved by encapsulation of one or both the pincer catalysts in the MOF UiO-66. A TON of 6600 was obtained for the hydrogenation (3 bar H_2) of CO_2 (37 bar) using a catalytic combination of RuPNN complex (**Ru-13**) and encapsulated RuPNP complex (**Ru-12**) [**Ru-12**]@UiO-66 in the presence of 2,2,2-trifluoroethanol (TFE) additive (10 mmol). Under the same conditions, a catalytic combination of RuPNP complex (**Ru-12**) and encapsulated RuPNN complex [**Ru-13**]@UiO-66 exhibited a slightly lower TON of 5700 (Figure 5). Moreover, when both the heterogenized complexes [**Ru-12**]@UiO-66 and [**Ru-13**]@UiO-66 were used, the TON was found to be just above half of that of [**Ru-12**]@UiO-66 + **Ru-13**. Interestingly, when both the pincer complexes were encapsulated in the same MOF - [**Ru-12, Ru-13**]@UiO-66, a better TON of 4300 was obtained (Figure 5). These heterogeneous systems were also successfully recycled for up to 5 times leading to a cumulative TON of 17,500-21,000. With this approach, the reaction could be performed in a single step and in one pot with high catalytic activity and recyclability of catalyst. Moreover, autocatalysis could also be possible as the final product methanol could be utilized for the esterification step.

In addition to methanol, the synthesis of higher alcohols (C2-C6) from CO_2/H_2 is also of significant interest because of their potential applications in fuels, additives, and as chemical feedstocks. However, producing higher alcohols from the hydrogenation of CO_2 is more challenging than producing methanol. Moreover, most of the catalysts reported for this transformation are heterogeneous in nature operating under harsh reaction conditions.[57] The first example of a homogeneous catalyst for hydrogenation of CO_2 to higher alcohols was reported by Tominaga and co-workers using a ruthenium-cobalt bimetallic system at 200 °C resulting in the formation of a mixture of methanol, ethanol, methane, and methyl formate.[81] Qian and Han reported that in the presence of a homogeneous bimetallic catalyst $Ru_3(CO)_{12}/Rh_2(CO)_4Cl_2$ with LiI as a promoter, CO_2 can be hydrogenated at 160°C to give a mixture of higher alcohols such as ethanol, propanol, 2-methyl propanol, butanol, and 2-methyl butanol in addition to methanol.[82] Higher activity was reported by replacing $Rh_2Cl_2(CO)_4$ with $Co_4(CO)_{12}$.[83] Utilizing the bimetallic catalyst $[RuCl_2(CO)_3]_2/Co_4(CO)_{12}$ and LiI as a promoter, the same group reported the efficient synthesis of ethanol using homologation of methanol using CO_2 and H_2.[84] Later, the same group reported that in the presence of a monometallic $Ru_3(CO)_{12}$ catalyst, ethanol can be synthesized under milder conditions (temperature 120 °C) with high selectivity from methanol and H_2 in the ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim]Cl), using LiCl and LiI as promoters.[85] The mechanistic studies revealed that RWGS reaction first produces CO which is subsequently consumed to form ethanol by methanol homologation reaction. Interestingly, the ionic liquid e.g. [bmim]Cl was also found to promote the RWGS reaction to generate a small amount of CO under reaction conditions. Ionic liquid also assisted in the regeneration of catalyst by allowing the removal of water (under vacuum at 80 °C) which was speculated to poison the catalysis. The catalyst could also be recycled with a TON of ethanol reaching 180 after five cycles.

Expanding on the catalytic applications of the bimetallic systems Qian and Han reported the selective synthesis of ethanol from the hydrogenation of paraformaldehyde using the bimetallic system of $Ru(acac)_3$ and $CoBr_2$ with LiI as a promoter in 1,3-dimethyl-2-imidazolidinone (DMI) under mild conditions.[86] A temperature of more than 140 °C was needed and the TOF (based on Ru metal) reached up to 17.9 h^{-1} at 180 °C. Based on the mechanistic investigations authors suggested that the reaction proceeds via (i) hydrogenation of paraformaldehyde to methanol, (ii) reverse water gas shift reaction, and (iii) methanol homologation to form ethanol. Later, in 2019, another catalyst system $Ru_3(CO)_{12}/Rh_2(CO)_4Cl_2$/LiI was reported to perform this transformation under relatively mild conditions.[84] Along this direction, the same group in 2018, reported a new strategy for the synthesis of ethanol from dimethyl ether, CO_2, and H_2 using Ru–Co bimetallic catalyst using LiI as a promoter in 1,3-dimethyl-2-imidazolidinone (DMI) solvent.[87] A high selectivity (up to 94.1%) of ethanol in the liquid products could be achieved. A more detailed review on the synthesis of higher alcohols (C1-C4) from $CO_2/CO/H_2$ using homogeneous catalysts has been recently reported by Klankermayer, Leitner, and Liauw.[88]

2.3 Formylation of amines using CO_2/H_2

Formamides are versatile chemicals and precursors for the synthesis of fine chemicals, natural products, and

pharmaceutically active compounds. For example, N, N-dimethylformamide (DMF) has applications in pharmaceutical, textile, and agrochemical industries. Thus, the utilization of CO_2 for the synthesis of formamides is relevant to circular chemistry. The reaction has been proposed to proceed via the hydrogenation of CO_2 to ammonium formate followed by thermal condensation to form formamide with the elimination of water (Figure 6).[27] The first report on the synthesis of DMF from the reaction of dimethylamine with CO_2 and H_2 dates back to 1969 by Haynes and co-workers.[89] The best results were obtained by cobalt and iridium phosphine complexes that exhibited a TON>1000. After this seminal discovery, several ruthenium-based homogeneous catalysts were reported for the synthesis of formamides from amines using CO_2 and H_2.[26,27] A highly active catalyst based on a Ru-Macho pincer complex (**Ru-14**, Figure 6) exhibiting TON of up to 1.94 million was reported by Ding for the N-formylation of various amines using CO_2 and H_2.[63] Moreover, recycling of the catalyst was also demonstrated for up to 12 cycles for the production of N, N-dimethylformamide without significant loss of activity. Tu has recently reported a solid molecular catalyst based on the iridium-NHC coordination assembly (**Ir-3**, Figure 6) for the N-formylation of a variety of amines using CO_2 and H_2.[90] A solid molecular catalyst allowed easy recovery of the catalyst by a simple filtration process that could be used more than 10 times without loss of activity for the production of DMF in solvent-free conditions.

In addition to precious-metal systems, a few homogeneous catalysts based on earth-abundant metals have also been reported for this transformation. Laurenczy and Beller in 2010 reported the first example of N-formylation of amines with a base-metal homogeneous catalyst $[FeH(H_2)(PP_3)]BF_4$, PP_3 = $P(CH_2CH_2PPh_2)_3$, generated in situ from $Fe(BF_4)_2{\cdot}6H_2O$ and the tetraphos ligand (PP3).[91] DMF, the only example, was produced in 75% yield with the catalyst's TON of 727 using this strategy. A more active iron catalyst, iron(II)-fluoro-tris(2-(diphenylphosphino)phenyl)phosphino]tetrafluoroborate which could be generated from the combination of $Fe(BF_4)_2{\cdot}6H_2O$ and a tetradentate phosphine ligand, tris(2-(diphenylphosphino)phenyl)phosphine was reported by Beller in 2012. This showed a TON of up to 5104 with a 74% yield of DMF.[92] A cobalt-based system using a precatalytic combination of $Co(BF_4)_2{\cdot}6H_2O$ and tetraphos ligand, $P(CH_2CH_2PPh_2)_3$ was used for the formation of DMF in 73% yield from NEt_3, CO_2 (30 bar) and H_2 (60 bar).[93] All these examples of base-metal catalysts were limited to the synthesis of DMF. Han and co-workers for the first time reported a base-metal catalyst based on $Cu(OAc)_2$-4-dimethylamino pyridine (DMAP) for the synthesis of a variety of formamides from the corresponding amines, CO_2 and H_2.[94] Remarkably, the catalyst was highly selective towards formylation even in the presence of unsaturated functional groups such as carbonyl groups, C=C, and C≡N bonds which were not affected under catalytic conditions (CO_2 and H_2 pressures of 40 bars each, temperature of 90 °C). Around a similar time, Milstein also reported a base-metal catalyst based on a cobalt pincer complex (**Co-1**, Figure 6) for the N-formylation of a variety of primary and secondary amines.[95] In all the catalytic systems reported to date, nucleophilic primary and secondary amines have been formylated with good to excellent yields, however, we do not find any examples of successful formylation of poor nucleophiles such as anilines and their derivatives.

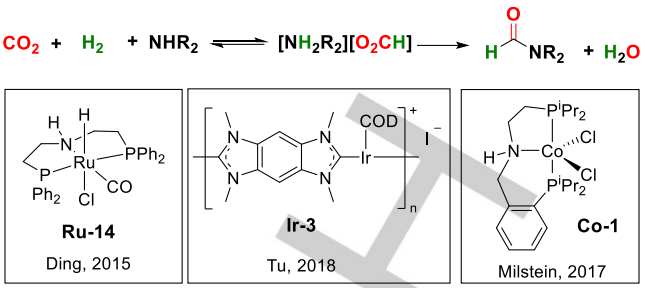


Figure 6. Catalysts for N-formylation of amines using CO_2/H_2.

Several examples of heterogeneous catalysts mostly based on precious metals have also been reported in recent years for the N-formylation of amines using CO_2/H_2.[96–98] However, pincer catalysts, for example, the one reported by Ding (TON of 1.94 million for the N-formylation of morpholine in 97 h at 120 °C and PCO_2 = PH_2 = 35 bar and that by Bernskoetter (TON = 4260 in 4 h at 120 °C and PCO_2 = PH_2 = 34.5 bar) still remain to be more active catalysts in this direction.

2.4 Methylation of amines, imines, and arenes using CO_2/H_2

Methylation is a highly useful strategy in organic synthesis, drug discovery, and materials science. Change of pharmacological properties upon the introduction of a methyl group in heteroarenes, also known as "magic methyl effect" has been well documented.[99] Nevertheless, most routes for methylation either use toxic reagents or produce stoichiometric amounts of waste creating a need for sustainable and green catalytic processes. Similar to formylation, the use of CO_2/H_2 for the purpose of methylation can be described as green and also may participate in a circular process to mitigate the excess CO_2. A mechanism for the N-methylation of amines proceeds first via the formation of formamides using CO_2/H_2 as discussed above (Figure 6), followed by deoxygenative hydrogenation of formamides to form N-methylated amines.[100] The later step has been reported by a few organometallic catalysts such as Ru-Triphos based systems which were utilized for N-methylation reaction.[101]

N-methylation of amines has been well studied by heterogeneous catalysts starting from the first report on this topic using a copper-alumina heterogeneous catalyst in 1995. Since then, several examples of heterogeneous catalysts using Ni, Pt, Pd, Co, Fe, Cu, Au, Al and Zr have been reported.[102–107] Recently, well-defined molecular complexes have also been utilized for the N-methylation reactions and will be discussed in the following section. In comparison to the homogeneous catalysts, heterogeneous catalysts have demonstrated better activity for N-methylation of amines under milder reaction conditions e.g. 10 bar CO_2 and 25 bar H_2.[107]

The first example for the homogeneously catalysed N-methylation of amines using CO_2/H_2 was reported by Klankermayer and Leitner in 2013 using a catalytic combination (**Ru-15**, Figure 7) of [Ru(triphos) (tmm)] (tmm = trimethylenemethane) and Bronsted acid cocatalyst trifluoromethanesulfonylimide ($HNTf_2$).[108] Several primary and secondary aromatic amines were N-methylated in good to excellent yields. As the dimethylaniline is found in many pharmaceutically active compounds, this path was also utilized to synthesize several N, N-dimethylaniline derivatives. Furthermore, a sequential hydrogenation/methylation strategy was

demonstrated to access unsymmetrical methyl/alkyl anilines from the corresponding amides. For example, acetanilide was converted to N-ethyl-N-methylaniline in a 69% yield in presence of CO_2/H_2 (20/60 bar) at 150 °C. Around a similar time, Beller also reported N-methylation of amines using an in-situ generated catalyst from the combination of $Ru(acac)_3$, triphos, and a Lewis or Bronsted acid (**Ru-16**, Figure 7).[109] Several aromatic amines were successfully N-methylated using the combination of $Ru(acac)_3$ (1 mol%), triphos (2 mol%), and methanesulfonic acid (MSA, 1.5 mol%). More nucleophilic aliphatic amines were methylated using Lewis acidic LiCl instead of a Bronsted acid such as MSA. This protocol was also applied for the selective monomethylation of aromatic diamines as well as to introduce a ^{13}C-methyl group in drugs containing amine functionality such as desipramine and nortriptyline. Along this line, Beller demonstrated dual substitution of anilines using the combination of RCOOH that performs alkylation (-transfer of R group) and CO_2/H_2 that performs the methylation in the presence of $Ru(acac)_3$, triphos and $HNTf_2$.[110]

Utilizing similar catalytic conditions as reported for the N-methylation of amines, Klankermayer and Leitner reported N-methylation of imines using CO_2/H_2 in the presence of [Ru(triphos)(tmm)] catalyst (**Ru-9**, Figure 4).[111] The synthetic application of this strategy was demonstrated by the atom-economic synthesis of an antifungal agent butenafine in one step.

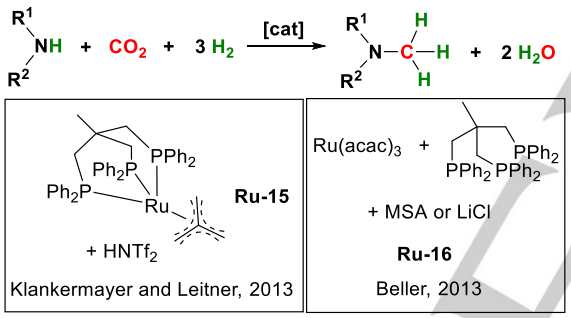
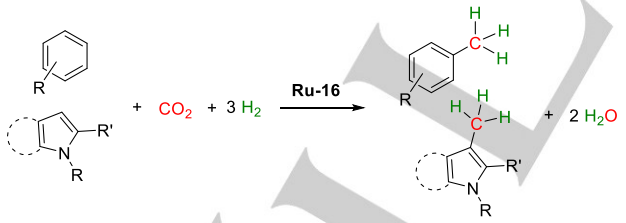


Figure 7. Catalysts for N-methylation of amines using CO_2/H_2.



Scheme 4. C-methylation of arenes using CO_2/H_2.

Similar to N-methylation of amines and imines, C-methylation of arenes using CO_2 and H_2 presents a green and attractive approach in organic synthesis, especially for functionalization of pharmaceutically active compounds. The first example for C-methylation of arenes using CO_2/H_2 was reported by Beller using $Ru(acac)_3$ in combination with triphos and MSA (**Ru-16**, Figure 7). [112] Several (hetero)arenes, such as indoles, pyrroles, and electron-rich arenes were C-methylated using CO_2 and H_2 (Scheme 4). Notably, this is the only example of a homogeneous catalyst reported to date for this type of transformation although some heterogeneous catalysts have also been reported recently.[113,114] A recent perspective report by Beller discusses the utilization of CO_2 for catalytic methylation reaction in more detail.[100]

2.5 Reaction of olefins with CO_2 and H_2

Olefins are useful feedstocks for a variety of reactions utilized in the industry such as alkoxy carbonylation and hydroformylation where olefins react with CO. Utilisation of CO_2/H_2 as a CO surrogate for its subsequent reactivity with olefins would be highly green and sustainable. The Reverse Water Gas Shift (RWGS) reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) has been mostly studied using heterogeneous catalysts due to the unfavourable thermodynamics (ΔH^o_{298} = 42.1 kJ/mol, ΔG^o_{298} = 28.5 kJ/mol).[115] The reported heterogeneous catalysts involve precious metals that are expensive leaving the room for development using active catalysts based on earth-abundant metals.[116]

An approach where the in-situ formed CO from the RWGS reaction can be trapped with olefins to form a more stable product has been utilized to overcome the thermodynamic barrier. Some homogeneous catalysts have demonstrated promising results in this direction recently (Figure 8). The first example in this direction was revealed by Sasaki in 2000 who reported the hydroformylation of cyclohexene using CO_2 (4.0 MPa) and H_2 (4.0MPa) in the presence of $H_4Ru_4(CO)_{12}$ and LiCl in NMP solvent.[117] The product hydroxymethyl cyclohexane was obtained in 88% yield (Figure 8A). Later in 2009, Haukka reported that oligonuclear and mononuclear ruthenium carbonyl species derived from $[Ru(CO)_4]_n$ can catalyse both RWGS reaction and hydroformylation reaction.[118] Using this catalyst, olefins were converted to alcohols in the presence of CO_2 and H_2 with similar catalytic activity as reported earlier by Sasaki (Figure 8B). Beller and Fleischer, in 2014 reported a more active catalyst based on $[Ru_3(CO)_{12}]$/phosphite (0.5 mol% each) that converted several olefins to alcohols using CO_2 (30 bar) and H_2 (30 bar) at 130 °C (Figure 8C).[119] A few other active catalysts for this transformation have been reported recently.[120,121]

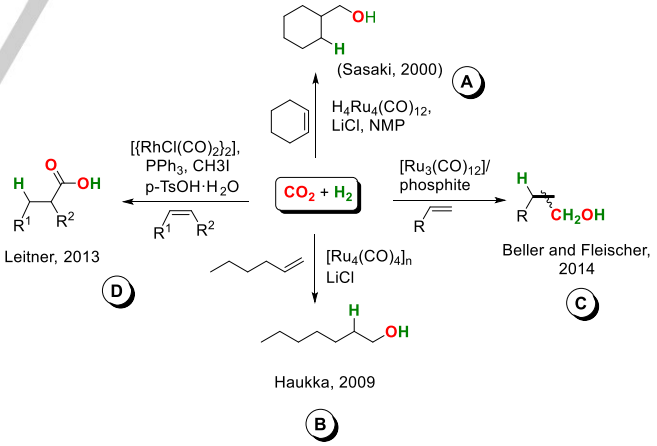


Figure 8. Reactions of olefins with CO_2/H_2 using homogeneous catalysts.

Other than alcohols, the RWGS reaction has been coupled with its reactivity with olefins to produce a carboxylic acid. Leitner reported catalytic hydrocarboxylation reaction using CO_2/H_2 in the presence of $[\{RhCl(CO)_2\}_2]$ and PPh_3 (Figure 8D). CH_3I was used as a promoter and p-TsOH·H_2O was used as an acid additive.[122] Several internal and terminal olefins were converted to carboxylic acids with good regioselectivities. Based on mechanistic studies, the authors suggest that the overall process is a combination of

rhodium-catalyzed RWGS reaction and hydroxycarbonylation cycles.

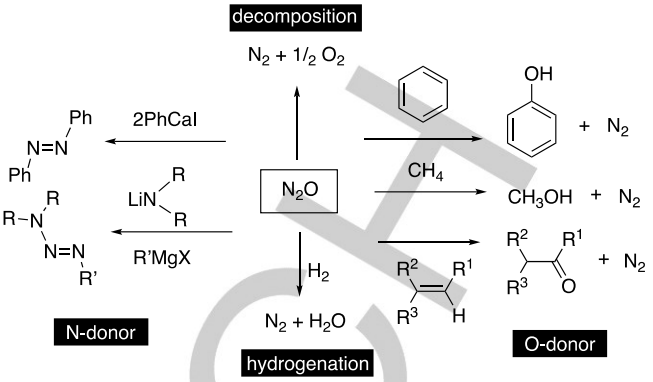
Carboxylic acids have also been shown to be prepared from hydrocarboxylation of alcohols using CO_2/H_2. Industrially, acetic acid is manufactured from Monsanto or Cativa process through the reaction of methanol with CO in the presence of a rhodium or iridium complex and HI. Qian and Han in 2016 reported hydrocarboxylation of methanol from CO_2 and H_2 to form acetic acid.[123] A bimetallic Ru-Rh catalyst bearing imidazole ligand was used as a catalyst and LiI was used as a promoter. Soon after, the same group reported the synthesis of acetic acid from methanol with CO_2 and H_2 using a simpler system based on $Rh_2(CO)_4Cl_2$ precursor and 4-methylimidazole (4-MI) in the presence of LiCl and LiI at 150 °C.[124] Recently, the same group reported the synthesis of higher carboxylic acids from ethers using the IrI_4 catalyst with LiI as a promoter at 170 °C, 5 MPa of CO_2, and 2 MPa of H_2.[125] More detailed reviews on the topic of carbonylation of alkenes using CO_2 have been reported by Beller[126] and Zhang[127] recently.

3. Hydrogenation of Nitrous oxide (N_2O)

Recent data show an upward increment in the atmospheric concentration of nitrous oxide gas (N_2O). Although, its atmospheric concentration (329.9 parts per billion in 2017) is substantially lower than that of CO_2 (405.5 parts per million in 2017), its effect on global warming is significantly higher (300 times that of CO_2).[128] Around 10-12 trillion grams of N_2O is emitted to the atmosphere annually from various sources such as agriculture (66%), energy and transport sector (15%), biomass burning (11%) and other processes (8%), and with the current emission rate, the amount of N_2O in the atmosphere is going to double by 2050.[129] Several methods have been reported for the removal or neutralization of N_2O such as (i) adsorption of N_2O on surfaces e.g. activated carbons and complex oxides which upon further treatment with steam can generate nitric acid and concentrated N_2O (ii) absorption of N_2O using various liquid absorbers from some of which it is possible to regenerate N_2O and (iii) catalytic decomposition or reduction of N_2O to N_2.[130]

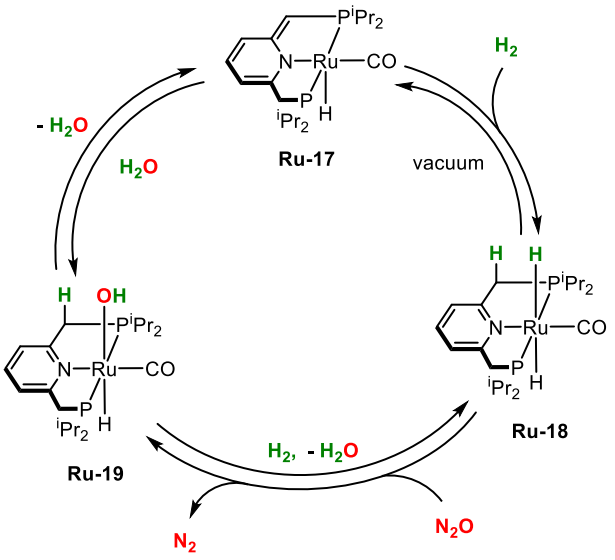
Although the decomposition of N_2O is thermodynamically downhill, a high barrier of N-O cleavage (+59 kcal mol^{-1} in the gas phase) makes the process kinetically unfavourable.[131] Because of the kinetic challenge, most of the examples in literature for the decomposition or reduction of N_2O involves heterogeneous catalysts such as transition-metal oxides at high temperature.[130]

The utilization of N_2O in organic synthesis is also of significant interest to mitigate the excess N_2O (Scheme 5). Heterogeneous catalysts have been employed to utilize N_2O for the synthesis of useful organic compounds. For example, Fe-containing ZSM-5 zeolites have been used for the synthesis of phenol by oxidation of benzene or its derivatives using nitrous oxide.[132] Similarly, the transference of 'O' atom from N_2O has been demonstrated for the synthesis of methanol from CH_4.[133] An interesting application of N_2O has been demonstrated for the synthesis of ketones from alkenes using a non-catalytic approach in the liquid phase.[134] N_2O has also been explored for the synthesis of azo-compounds (Scheme 5). Applications of N_2O as a reagent in organic synthesis has been recently reviewed by Severin.[135]



Scheme 5. Conversion of N_2O to valuable chemicals.

Neutralization of N_2O using hydrogen gas as a reductant has also been attempted. Seminal reports on the hydrogenation of N_2O has been reported using heterogeneous catalysts at temperatures of 250-500 ˚C.[136–138] As homogeneous catalysts can enable a reaction to occur under milder conditions, several transition-metal-complexes have been studied for this purpose. Early works on hydrogenation of N_2O to water ($N_2O \rightarrow N_2 + H_2O$) using a transition-metal complex have been reported by Bergman,[139] Caulton[140] and Piers.[141] However, in all the cases only stoichiometric activities were reported. The first and the only example for the catalytic hydrogenation of N_2O using a homogeneous catalyst has been reported by Milstein using a ruthenium PNP pincer complex.[142] Screening several ruthenium pincer catalysts for the hydrogenation of N_2O (13 mmol of H_2 in 5 mL of N_2O in THF) revealed the dearomatized RuPNP complex, **Ru-17** (Scheme 6) to be a highly active catalyst resulting in 220 TONs at 65 °C in 36 h. Complex **Ru-17** was found to be converted to a new ruthenium hydride hydroxy complex **Ru-19** after the reaction. Interestingly, **Ru-19** exhibited even a higher TON of 307 at 65 °C in 37 h. A mechanism was proposed using NMR spectroscopy according to which the dearomatized complex **Ru-17** reacts with H_2 gas to form a *trans*-dihydride complex **Ru-18** that performs mono oxygen transfer of N_2O to form a ruthenium hydride hydroxo complex **Ru-19** liberating N_2 (Scheme 6). Complex **Ru-19** can eliminate H_2O via metal-ligand cooperation to regenerate the dearomatized complex **Ru-17**. The involvement of complex **Ru-18** in the catalysis was further confirmed by using it for the catalytic hydrogenation reaction. The results showed that complex **Ru-18** was the most active catalyst for the hydrogenation of N_2O. Detailed mechanistic studies have been reported using DFT by the groups of Poater[143] and Xie[144] who suggest that H_2O plays an important role in the overall hydrogenation process by lowering the barrier of the oxygen transfer step (**Ru-18** → **Ru-19**).



Scheme 6. Catalytic hydrogenation of N_2O using a ruthenium pincer complex.

4. Depolymerisation of plastics using catalytic (de)hydrogenation

Our growing dependence on plastics has resulted in their increased production over the years. Their omnipresence and non-biodegradable nature have caused intense plastic pollution, both on land and in oceans resulting in grievous threats to our biosphere.[145][146] Two approaches have been used to tackle this global challenge: (a) making biodegradable plastic, and (b) recycling current plastic waste. Currently, recycling of plastic is mostly done via mechanical recycling where plastic is mechanically (such as melting and re-extrusion) converted to other usable forms of plastic.[147] However, this method suffers from drawbacks such as each time plastic is mechanically recycled, its quality degrades, and therefore a plastic can only be mechanically recycled a few times before it ends up in a landfill. Because of this, all the plastic produced to date, apart from those incinerated or chemically degraded, still stays in the form of plastic. Thus, mechanical recycling is not a sustainable mode of recycling as it only increases the lifetime of plastic rather than degrading it to its original form. The only sustainable mode of plastic recycling is chemical recycling where a plastic is converted to (a) its monomer from which the same virgin plastic can be made, or (b) useful building blocks that can be used as a chemical feedstock.[148–150] Several methods have been explored for the chemical recycling of plastics such as pyrolysis, hydrolysis, glycolysis, and aminolysis.[149] However, these methods suffer from the drawbacks of harsh reaction conditions (e.g. temperature > 250 °C) and low selectivity. Furthermore, in several cases, pyrolysis and glycolysis do not result in the same monomer which can be used to produce fresh plastic. Approach based on catalytic (de)hydrogenation has been recently utilized for the depolymerisation of plastics and is the focus of this review.

Reactions based on (de)hydrogenation pathways have been used for both the synthesis and degradation of small molecules to form a closed-loop production cycle. For example, esters can be synthesized from the dehydrogenative coupling of alcohols and the same alcohols can be regenerated from esters via the reverse reaction i.e. catalytic hydrogenation reaction (Figure 9A).[12,151] Similarly, amides can be produced from the dehydrogenative coupling of alcohols and amines, and the same alcohols and amines used in the first place can be regenerated back from the catalytic hydrogenation of amides. This unique quality of (de)hydrogenation reactions can also be exploited to develop closed-loop production cycles of plastics such as polyesters and polyamides (Figure 9B). In the direction of the plastic synthesis using catalytic dehydrogenation process, Robertson reported the synthesis of high molecular weight polyesters from the dehydrogenative coupling of diols using Milstein's RuPNN pincer catalyst (**Ru-20**, Figure 9C).[152] Using the same RuPNN pincer catalyst (**Ru-20**), Guan[153] and Milstein[154] independently reported the synthesis of polyamides from the dehydrogenative coupling of diols and diamines (Figure 9C). Later, Keul and Moller reported a dehydrogenative synthesis of polyesters and polyamides using an N-heterocyclic carbene ruthenium complex.[155] The reverse reaction i.e. hydrogenative depolymerisation of polyesters and polyamides have also been reported and is discussed in the following sections. Overall, using catalytic (de)hydrogenation pathways, it is possible to achieve the closed-loop production of plastics.

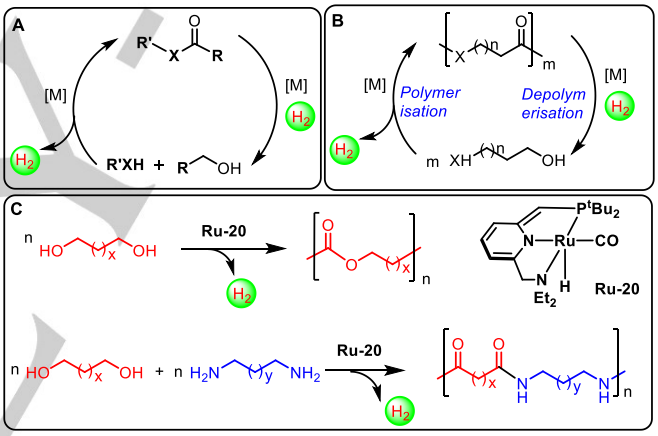


Figure 9. Closed-loop production of esters/amides (A) and polyesters/polyamides (B) using catalytic (de)hydrogenation routes (X = O, NH), and synthesis of polyesters and polyamides using a ruthenium pincer catalyst (C).

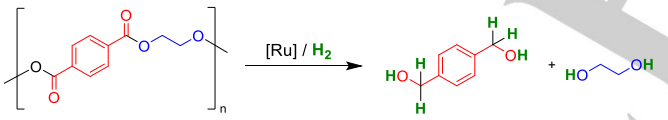
The approach of catalytic hydrogenation has been employed for the depolymerisation of polyesters, polycarbonates, and nylons as discussed in the following sections. Such reactions have not been accomplished yet using a heterogeneous catalyst and the state-of-the-art catalytic methods are dominated by well-defined transition-metal-complexes.

4.1 Hydrogenative depolymerisation of polyesters

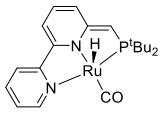
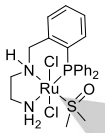
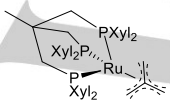
With the global production of more than 50 million tons, polyesters, the most common of which is PET (polyethylene terephthalate), are commonly used plastics with applications in textiles, packaging, and electronics industries.[156] Earlier reports on the chemical recycling of polyesters involve methanolysis, hydrolysis, glycolysis, and aminolysis, which have been well-reviewed in the past.[157,158] Steady progress has also been made in the past few years regarding the degradation of polyester (waste) using the approach based on catalytic hydrogenation. The first example of catalytic hydrogenation of polyesters was

reported in a patent by Milstein in 2013.[159] Soon after that, in 2014, Robertson reported hydrogenative depolymerisation of polyesters into diols using Milstein's Ru(II) PNN complexes **Ru-20** (Figure 9) and **Ru-5** (Table 1).[160] Linear aliphatic polyesters were successfully depolymerised to the corresponding diols with around 80% yield in the presence of complex **Ru-20** and hydrogen gas (13.6 atm, 120 °C for 48 h). However, catalyst **Ru-20** was ineffective for the hydrogenation of caprolactone and PET which were achieved using RuPNNbipy catalyst **Ru-5** (Table 1). To ensure solubility of partially depolymerised products a 50:50 ratio of anisole: THF was used as a solvent along with an elevated temperature. The PET was sourced from a used water bottle, which demonstrated the tolerant nature of the catalysts towards impurities and commercial additives. Higher activity of complex **Ru-5** was attributed to the less sterically bulky dipyridyl backbone compared to the dimethylamino methyl arm on complex **Ru-20**. Catalyst **Ru-5** was also able to hydrogenate polylactic acid (PLA) to polyethylene glycol with full conversion under the same conditions as that of PET. Surprisingly, polyesters such as polyhydroxybutyrate (PHB) and poly(3-hydroxypropionic acid) (P3HP), with three or four methylene units, depolymerised to give carboxylic acids rather than diols. Depolymerisation of enantiomerically pure polyhydroxybutyrate (PHB) using catalyst **Ru-5** afforded butyric acid in 88% yield as the only product instead of the expected enantiomerically pure *R*-1,3-butanediol. Similarly, P3HP was depolymerised to propionic acid with a 90% conversion using catalyst **Ru-5**. The reason that carboxylic acids formed instead of diols is currently uncertain. A plausible mechanism could be via deprotonation of CH_2 proton adjacent to the ester (CH_2-OC=O) group and elimination of but-3-enoic acid followed by hydrogenation of C=C bond to form butyric acid. Repetition of this step could result in the depolymerisation of polyhydroxybutyrate to butyric acid.

Table 1. Hydrogenative depolymerisation of PET.



Polyethylene terephthalate (PET)

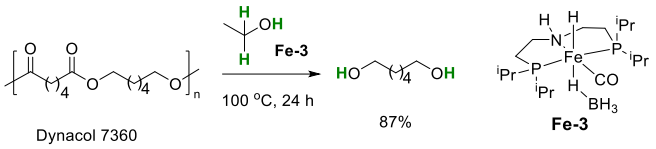
Entry	Catalyst	Conditions	% Yield
1	 **Ru-5** Robertson, 2014	54.4 atm hydrogen gas, 160 °C, 50:50 mixture of THF:anisole	>99
2	 **Ru-21** Clarke, 2015	50 bar hydrogen gas, 110 °C, 50:50 mixture of THF:anisole,	73
3	 **Ru-22** Klankermayer, 2015	100 bar hydrogen gas, 140 °C, $HNTf_2$ cocatalyst, 1,4-dioxane	>99

After seminal reports by Milstein and Robertson, hydrogenative depolymerisation of PET was demonstrated by Clarke using a range of tridentate aminophosphine ruthenium complexes.[161] Out of seven pre-catalysts, complex **Ru-21** (Table 1) was found to exhibit the best performance for hydrogenation of two model diesters. This prompted a further study on the performance of complex **Ru-21** towards the hydrogenative depolymerisation of PET flakes. Similar to Robertson's initial work, anisole was used as a co-solvent in a 50/50 mixture of toluene/anisole to improve polymer solubility. Under 50 bar of hydrogen gas and at 110 °C, 73% conversion of PET to 1,4-benzenedimethanol was obtained.

In 2018, Klankermayer reported hydrogenative depolymerisation of a range of polyesters to diols using the [Ru(triphos)tmm)] (**Ru-9**, Figure 4) and [Ru(triphos-xyl)tmm)] catalysts (**Ru-22**, Table 1).[162] Full conversion of polylactic acid (PLA) to 1,2-propanediol was achieved with 1 mol % [Ru(triphos)tmm)] (**Ru-9**) catalyst and bis(trifluoromethanesulfonyl)imide ($HNTf_2$) cocatalyst at 140 °C in 1,4-dioxane. Polycaprolactone (PCL) was also hydrogenated (complete conversion) to produce 1,6-hexanediol as the only product. Hydrogenative depolymerisation of PET was found to be more challenging. [Ru(triphos)tmm)] (**Ru-9**) exhibited only 42% conversion of PET with 64% selectivity towards 1,4-benzene dimethanol and ethylene glycol. Polybutylene terephthalate (PBT) was also converted to 1,4-benzene dimethanol and 1,4-butanediol using [Ru(triphos)tmm)] (**Ru-9**) with only 22% selectivity. Reduced selectivity for PET and PBT was due to further reactions to form ethers favoured by the acid-activated catalyst. To enhance the yields for the hydrogenative depolymerisation of PET and PBT, a modified ruthenium catalyst, [Ru(triphos-xyl)tmm)] (**Ru-22**) was used. This catalyst showed higher stability and activity, resulting in full conversion of PET with 64% selectivity to the corresponding diols in the presence of 1 mol% catalyst loading and $HNTf_2$ as a cocatalyst at 140 °C in 1,4-dioxane. PBT also showed complete conversion under the same conditions, with a selectivity of >99% towards respective diols. Using this established catalyst system, hydrogenation of commercially available PET flakes from an untreated water bottle was also demonstrated that showed full conversion with excellent selectivity, even at 0.2 mol% catalyst loading. Following this success, the reaction was carried out on PET flakes from a dyed soda bottle, synthetic pillow filling, and yoghurt pots using swollen polymers to improve solubility. Complete conversion of all the consumer products tested at 0.5 mol% catalyst loading resulted in the formation of diols with excellent selectivity. The lack of pre-treatment of the PET highlights the tolerance of this catalyst to commercial additives and pigments. Hydrogenative depolymerisation processes of various consumer products made from polyesters (PLA and PET) and a polycarbonate were also demonstrated on gram scale affording excellent yields of corresponding diols with conversion and selectivity (>99%).

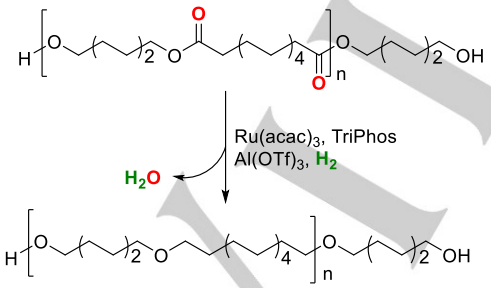
In addition to the ruthenium complexes, a base-metal catalyst based on a Fe-Macho complex (**Fe-3**) has been utilized by de Vries and co-workers for the depolymerisation of polyesters, although using transfer hydrogenation pathway, unlike the above discussed three catalysts that use molecular hydrogen for the depolymerisation process.[163] Remarkably, EtOH, a renewable feedstock, was used as a hydrogen source compared to the conventionally used isopropanol. In the presence of 5 mol% Fe-Macho complex (**Fe-3**), Dynacol 7360 which is made from adipic

acid and 1,6-hexanediol, was depolymerised to form 1,6-hexanediol in 87% yield at 100 °C in 24 h (Scheme 7).



Scheme 7. Transfer hydrogenation of polyester using an iron-pincer catalyst.

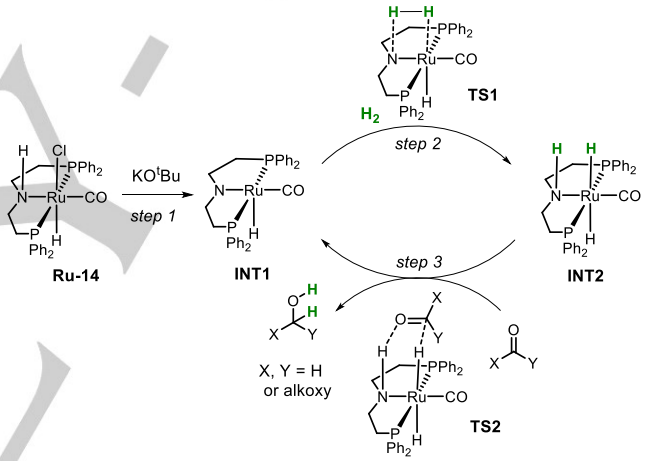
Recently de Vries and co-workers have reported an alternative strategy for the recycling of polyesters via catalytic hydrogenation (Scheme 8).[164] Authors utilized a ruthenium-triphos complex as they were earlier demonstrated for the direct reductive etherification of carboxylic acid esters to ethers.[165,166] Catalytic hydrogenation was performed using $Ru(acac)_3$ (1 mol%) precatalyst, Triphos ligand (1.5 mol%), and a Lewis acid as a cocatalyst. The Lewis acid plays a dual role in catalysis by (a) activating the catalyst, and (b) catalysing the etherification step. In support of the latter role, when a catalytic hydrogenation reaction was performed using a 1:1 ratio of $Ru(acac)_3$ and the Lewis acid $Al(OTf)_3$, no ether linkage was obtained despite the full conversion of polyester, and only free diols were detected. This suggests that an additional amount of a Lewis acid is needed for the etherification step. Optimization of catalytic conditions revealed that the best activity was obtained in THF, 140 °C, 40 bar H_2, 24 h in the presence of $Al(OTf)_3$ as a cocatalyst. The ratio of the loading of $Ru(acac)_3$ and $Al(OTf)_3$ also showed effects on the catalytic activity. In the presence of a higher concentration of ruthenium, increasing the $Al(OTf)_3$ amount resulted in a lower conversion of the polyester whereas at a lower concentration of ruthenium, increasing the $Al(OTf)_3$ amount resulted in a higher conversion of the polyester. Based on mechanistic investigations such as monitoring molecular weights during catalysis and control experiments, a tandem two step-pathway involving ruthenium catalysed hydrogenation of polyesters to diols followed by Lewis acid catalysed etherification of diols to polyethers was proposed. The strategy was also extended for the hydrogenation of a broader substrate scope of polyesters.



Scheme 8. Ruthenium catalysed hydrogenation of polyesters to polyethers.

4.2 Hydrogenative depolymerisation of polycarbonates

Although less than polyesters, polycarbonates (PC) are also commonly used plastics with an annual global demand of more than 4.3 million tons with applications in the production of electronic components and construction materials.[167] Several approaches such as solvolysis, hydrolysis, methanolysis, alcoholysis, and glycolysis where PC waste is heated in the presence of a solvent/reagent at high temperature (>300 °C), have been explored for the degradation of PC.[168] With the advancement in the robust and active (de)hydrogenation catalysts, in recent years, a few examples for the hydrogenative depolymerisation of PC has also been reported. The first report on the hydrogenative depolymerisation of PC was made by Ding and co-workers in 2012.[169] In the presence of a ruthenium-Macho complex **Ru-14** (15.8 mg, 0.1 mol %), KO^tBu (1 mol%) and 50 bar H_2 (140 °C, 24 h), a sample of poly(propylene carbonate) (PPC; 2.69 g) with a weight-average molecular weight (Mw) of 100698 (Mw/Mn=1.77, >99% carbonate linkages) was depolymerised to form methanol and 1,2-propylene glycol in an almost quantitative yield. A proposed mechanism is outlined in Scheme 9. The precatalyst **Ru-14** in the presence of KO^tBu forms the active species INT1 that activates H_2 to form the ruthenium *trans*-dihydride species INT2 via a transition state (TS1). INT2 hydrogenates the C=O bond of the carbonate group via an outer-sphere mechanism to form an orthoformate intermediate through a transition state (TS2) that further goes to form a formate intermediate. The formate intermediate undergoes the same cycle to form diols and methanol.

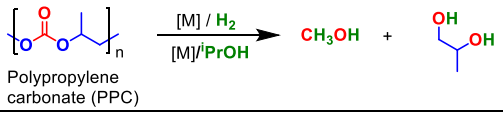


Scheme 9. Proposed catalytic cycle for the hydrogenation of a carbonate group by a ruthenium pincer complex **Ru-14**.

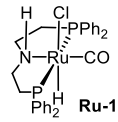
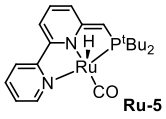
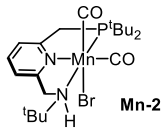
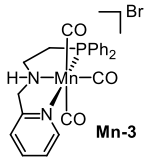
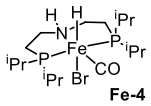
Later in 2014, Robertson and co-workers used the Milstein RuPNN pincer catalysts **Ru-20** (Figure 9) and **Ru-5** (Table 2) for the hydrogenative depolymerisation of polypropylene carbonate and polyethylene carbonate.[160] In the presence of 1 mol% ruthenium precatalyst and 2 mol% KO^tBu under 54.4 bar of H_2 at 160 °C, almost complete degradation of polycarbonates was observed to form a mixture of the corresponding diol and methanol in more than 99% yield. A solvent mixture of anisole and THF was used for solubility purposes. Recently, Klankermayer has also demonstrated hydrogenative depolymerisation of commercial PC using [Ru(triphos)tmm] and bis(trifluoromethanesulfonyl) imide ($HNTf_2$) (**Ru-15**, Figure 7) as a catalyst system at 140 °C and 100 bar H_2 pressure in the 1,4-dioxane solvent.[162] Poly(bisphenol A carbonate), which is the most common type of polycarbonate, was hydrogenated to produce bisphenol A and methanol in an almost quantitative yield. Moreover, consumer products such as a compact disc (CD) and a regular beverage cup were hydrogenated to form the corresponding diols in quantitative yields in the presence of only 0.33 mol % [Ru(triphos)tmm]/$HNTf_2$ catalyst (**Ru-15**, Figure 7). Remarkably, the impurities present in consumer products such as

labeling dye, aluminum coating, or metallic glitter did not affect the catalysis.

Table 2. Hydrogenative depolymerisation of polypropylene carbonate using homogeneous catalysts.



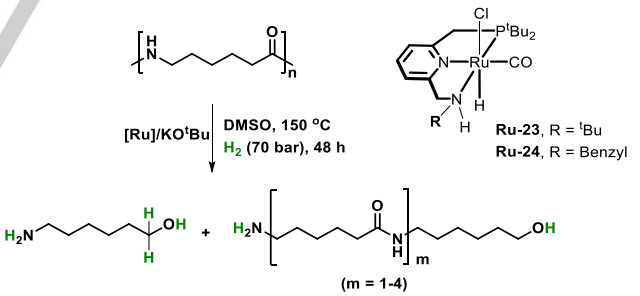
Polypropylene carbonate (PPC)

Entry	Catalyst	Conditions	% Yield (methanol and diol)
1.	 **Ru-14** Ding, 2012	**Ru-13** (0.1 mol %), KO^{t}Bu (1 mol%), 50 bar H_2 (140 °C, 24 h), THF	99% each
2.	 **Ru-5** Robertson, 2014	54.4 bar H_2,160 °C, 50:50 mixture of THF:anisole	>99% each
3.	 **Mn-2** Milstein, 2018	**Mn-2** (2 mol %), KH (4 mol%) 50 bar H_2 (110 °C, 50 h), toluene	59% methanol 68% diol
4.	 **Mn-3** Rueping, 2018	**Mn-3** (1 mol %),KO^{t}Bu (2.5 mol%), 50 bar H_2 (140 °C, 16 h), 1,4-dioxane	84% methanol 91% diol
5.	 **Fe-4** Werner, 2019	**Fe-4** (5 mol %),KO^{t}Bu (5 mol%) ^{i}PrOH (140 °C, 30 h), THF	43% methanol 65% diol

In addition to ruthenium catalysts, catalysts based on earth-abundant metals have also been exploited for the hydrogenative depolymerisation of PC. Milstein and Rueping around a similar time in 2018 reported hydrogenative depolymerisation of PPC using manganese pincer catalysts (Table 2). In the case of the Milstein's system, a catalytic combination of Mn-PNNH complex **Mn-2** (2 mol%, Table 2) and KH (4 mol%) performed hydrogenative depolymerization of PPC under 50 bar of H_2 and at 110 °C (toluene solvent) temperature to afford propylene glycol and methanol in 68% and 59% yields, respectively.[170] In comparison, the Rueping system that used the Mn-PNN complex **Mn-3** (1 mol%, Table 2) and KO^{t}Bu (2.5 mol%) at 140 °C, 16 h, and 50 bar H_2 (1,4-dioxane solvent) afforded better yields of the corresponding diol (91%) and methanol (84%).[171] In addition to manganese, an iron pincer catalyst has also been recently utilized for the depolymerisation of PPC via transfer hydrogenation (Table 2). Werner, in 2019, reported that in the presence of a Fe-PNP Macho complex (**Fe-4**, 5 mol%, Table 2) and KO^{t}Bu (5 mol%), commercially available PPC (Mn = 50,000 g/mol) was hydrogenated using ^{i}PrOH as a hydrogen source to afford propylene diol and methanol in 65% and 43% yields respectively.[172] Interestingly, performing a transfer hydrogenation reaction in the absence of the iron complex and in the presence of 5 mol% KO^{t}Bu also resulted in the depolymerisation of the PPC. The products were identified as a mixture of cyclic carbonate and propylene glycol, which could come from the transesterification of the PPC with isopropanol. Based on this observation, authors speculate that partial depolymerisation of PPC is possible just in the presence of a catalytic amount of a base.

4.3 Hydrogenative depolymerisation of nylons and polyurethanes

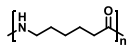
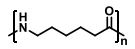
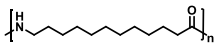
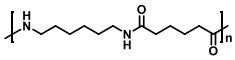
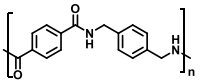
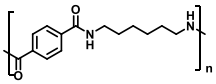
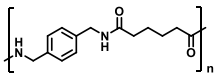
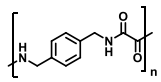
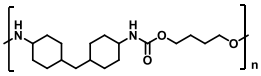
More than 8 million tons of nylons are currently produced globally with an estimation of reaching up to 10.4 million tons by 2027.[173] Like polyesters and polycarbonates, several approaches such as pyrolysis, hydrolysis, aminolysis, and glycolysis have been explored for the chemical degradation of nylon waste.[174,175] An approach based on catalytic hydrogenation for the chemical recycling of nylons or polyamides has been revealed very recently by Milstein and co-workers using ruthenium pincer complexes.[176] Compared to polyesters and polycarbonates, nylons are more difficult to hydrogenate using a homogeneous catalyst due to the presence of relatively stronger intermolecular hydrogen-bonding that makes nylons insoluble in common solvents. The solvent screening revealed that DMSO was the optimum solvent that could dissolve nylons at high temperatures and also allow the catalytic hydrogenation to occur without binding to the active site. Best catalytic activity was obtained by ruthenium pincer complexes **Ru-23** and **Ru-24** (2 mol%) with KO^{t}Bu (8 mol%) under 70 bar of H_2 at 150 °C that depolymerised commercial resins of nylon 6 (conversion 70-80%) to form 6-amino-1-hexanol in 24-26% yield, the rest being oligoamides (dimer to tetramer) as confirmed by the GC, NMR spectroscopy and mass spectrometry (Scheme 10).



Scheme 10. Ruthenium catalysed hydrogenative depolymerisation of nylon 6.

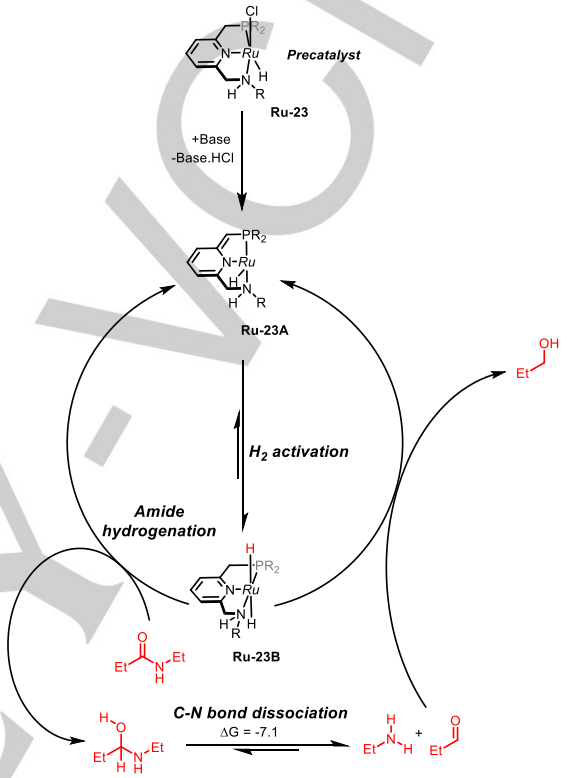
Quantitative conversion of nylon 6 (99%) was obtained using a dual hydrogenation approach where after the first hydrogenation step the catalyst was recharged and the autoclave was pressurized with 70 bar of H_2 and heated at 150 °C for 72 h resulting in 37% yield of 6-amino-1-hexanol. Authors observed that 1,4-dioxane is a better solvent than DMSO for the hydrogenation of an amide bond, however, DMSO is needed for dissolving nylon 6. Thus, a higher yield of 6-amino-1-hexanol (48%) was obtained using a dual approach where after the first step of hydrogenation in DMSO, DMSO was removed and the residue was hydrogenated again in 1,4-dioxane solvent after the addition of the fresh catalyst. Other nylons such as nylon 12 and

Table 3. Hydrogenative depolymerisation of nylons. Reproduced with permission from reference 176. Copyright American Chemical Society.

Entry	Polymer	Form	Mol Wt	Conversion	Yield of amino alcohols, diols/diamines
1.		resins	10,000	77% 99%[b] 80%[c]	24% 37%[b] 48%[c]
2.		powder	11,000	85% 99%[d]	36% 55%[d]
3.		resins[e]	-	80%	30%
4.		powder	3500	60%	20% (diol) 25% (diamine)
5.		powder	1500	99%	80% (diol) 85% (diamine)
6.		powder	4500	80%	42% (diol) 45% (diamine)
7.		powder	2500	95%	75% (diol) 74% (diamine)
8.		powder	1500	95%	77% (diol) 82% (diamine)
9.		resins[e]	-	90%	70% (diol) 66% (diamine)

[a]Catalytic conditions: Polyamide (1 mmol relative to the molecular weight of the monomer), complex **Ru-23** (0.02 mmol), KO^{t}Bu (0.08 mmol), DMSO (2.5 mL), H2 (70 bar), temperature 150 ^{o}C and reaction time 48 h. [b]Two sequential hydrogenation steps both in DMSO. [c]Two sequential hydrogenation steps first in DMSO and second in 1,4-dioxane. [d]**Ru-24** (0.05 mmol) and KO^{t}Bu (0.2 mmol), 72 h, remaining conditions as above[a]. [e]Molecular weight could not be determined.

nylon 66 as well as polyamides containing aliphatic and aromatic moieties were also successfully depolymerized (Table 3). Furthermore, a polyurethane was also hydrogenated to form a mixture of diol, diamine, and methanol. It is noteworthy that polyurethane can be synthesized from CO_2 thus this route also represents a proof of concept for the hydrogenation of waste polyurethane (plastic) to a useful chemical and fuel - methanol. In addition, a closed-loop chemical recycling of polyamide was also demonstrated where the monomers obtained from the hydrogenative depolymerisation step was converted back to a polyamide of the same bond-linkage and a similar molecular weight by a ruthenium catalysed dehydrogenation process. Based on experiments and DFT calculations, a mechanism as outlined in Scheme 11 was proposed. The precatalysts **Ru-23** first reacts with a base to form the dearomatized complex **Ru-23A** which in the presence of a hydrogen atmosphere gets transformed into a ruthenium *trans* dihydride complex **Ru-23B**. Complex **Ru-23B** was spectroscopically characterised and found to be stable under an H_2 atmosphere. Insertion of an amide bond to the Ru-H of **Ru-23B** leads to the formation of a hemiaminal intermediate regenerating **Ru-23A** via metal-ligand cooperation. Decomposition of the hemiaminal intermediate results in the formation of an amine and an aldehyde. The aldehyde gets hydrogenated by **Ru-23B** to form an alcohol and regenerates **Ru-23A**. Calculations suggested that hydrogenation of amide bonds occurs via Noyori's stepwise outer-sphere mechanism where the hydride transfer precedes the proton transfer step. The dual role of KO^{t}Bu was suggested that facilitates the (a) generation of a dearomatized complex, which is the active species, from the precatalyst, and (b) decomposition of hemiaminal intermediate to aldehyde and amine. The experiments suggested that the main role of the DMSO was to dissolve nylons and DMSO is not involved in the catalytic cycle.



Scheme 11. Proposed mechanism for the hydrogenative depolymerisation of nylons using pincer complexes **Ru-23**,**24**. Reproduced with permission from reference 176. Copyright American Chemical Society.

4.4 Conversion of polyethylene to fuel using cross alkane metathesis

Polyethylene (PE) is the most commonly used plastic with a global production of more than 100 million tons accounting for around 34% of the total plastic production in the world.[145] The non-polarizable chain and absence of any functional group make PE chemically inert and most of the studies on chemical recycling of PE are based on pyrolysis (direct or catalytic) or hydrothermal processes using strong oxidizing agents such as HNO_3.[145] Pyrolysis processes have the drawback of producing a random complex polymeric mixture of products, and it is not surprising that only two examples of the chemical recycling of PE on a commercial scale have been demonstrated.[177,178] An approach based on catalytic (de)hydrogenation/metathesis has also been explored for the depolymerisation of PE. The concept, commonly known as cross alkane metathesis (CAM), developed by Goldman and Brookhart, is a tandem process involving (i) dehydrogenation of alkanes (a long chain and a light alkane) to

olefins in the presence of a pincer catalyst (ii) metathesis of the generated olefins catalysed by a metathesis catalyst forming new olefins of varied chain length, and (iii) hydrogenation of generated olefins in the presence of the same pincer catalyst used earlier for dehydrogenation, to produce alkanes of smaller chain length.[179] This concept was utilized by Guan and Huang for the depolymerisation of PE, which can be treated as a long alkane chain, to produce liquid fuels and waxes (Figure 10A).[180] Utilizing an iridium PCP catalyst **Ir-4** (Figure 10B) for (de)hydrogenation and $Re_2O_7/\gamma\text{-}Al_2O_3$ for metathesis resulted in a 56% degradation of HDPE (powder; weight-average molecular weight (Mw) = 3350; polydispersity index (PDI), 1.6) to oil products ($C_{22\text{-}40}$) using hexane as a light alkane for cross-metathesis. It is noteworthy that for a PE chain to degrade, the metathesis of an internal double bond is required. Therefore, a higher degradation (up to 98% to oil) of PE was observed when Brookhart's bis(phosphinite)-ligated (t-BuPOCOP)Ir complexes (**Ir-5,6**, Figure 10B) were used, which are known for the selective formation of internal olefin, rather than a terminal olefin upon dehydrogenation.

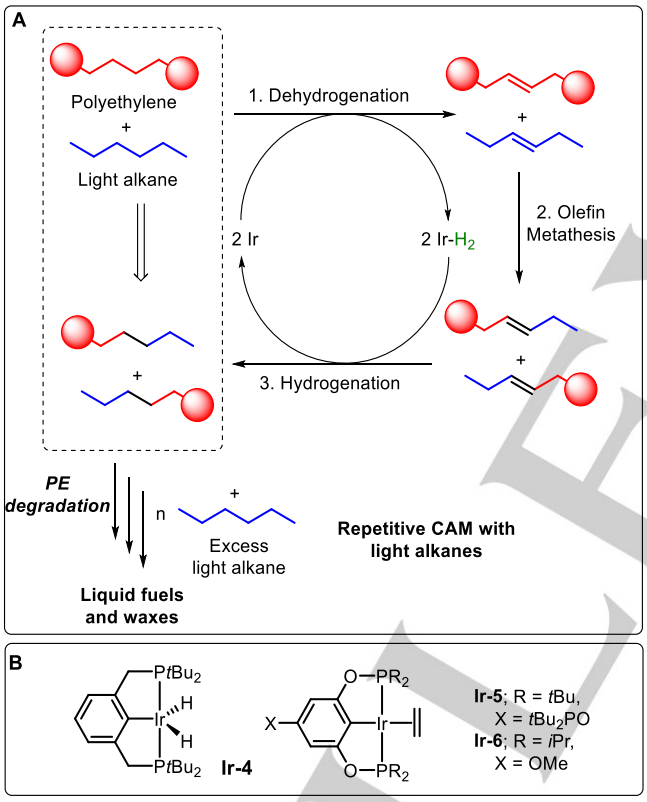
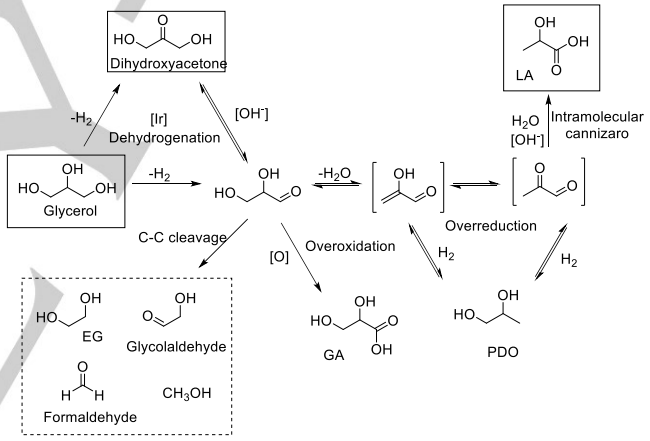


Figure 10. A. Cross-alkane metathesis (CAM) between polyethylene and a light alkane (n-hexane); **B**. Iridium pincer catalysts used for (de)hydrogenation steps.

The practicality of this methodology was also demonstrated by degrading common plastic wastes without any pre-treatment such as post-consumer polyethylene bottles, bags, and films.

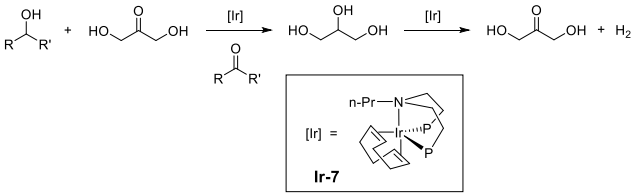
5. Dehydrogenation of glycerol

Glycerol is a cheap and renewable feedstock that is being produced as a by-product of the soap and biodiesel industry. Although glycerol has several applications such as in the food and medical industries, due to the recent increase in biodiesel production, the supply of glycerol has become higher than its demand.[181] With the recent trend of biodiesel production because of its rising popularity as an alternative energy source of fossil fuel, the overproduction of glycerol is going to continue in the future. This creates urgent opportunities to utilise glycerol as a feedstock to produce useful chemicals. Utilization of glycerol for value-added products such as propanediol, acrolein, dihydroxyacetone (DHA), glyceric acid (GA), and cyclic acetals or epichlorohydrin has been reviewed in the recent past.[182–185] An important application is the production of syngas ($CO+H_2$) from the glycerol reforming reaction in the presence of heterogeneous catalysts. Another interesting application is the production of hydrogen gas from the steam reforming of glycerol ($C_3H_8O_3 + 3H_2O \rightarrow 3\ CO_2 + 7H_2$). However, due to unfavourable thermodynamics (ΔH = 128 kJ/mol), the reaction is performed at a very high temperature (800 °C) in the presence of heterogeneous catalysts.[186] Several homogeneous catalysts have been utilized for the dehydrogenation of glycerol under mild conditions for the purpose of both hydrogen storage and organic synthesis as discussed in the following section. Various products such as dihydroxyacetone (DHA), glyceraldehyde (GAL), 1,2-propanediol (PDO), glyceric acid (GA), and lactic acid (LA) can be produced from dehydrogenation type reactions of glycerol (Scheme 12).



Scheme 12. Possible dehydrogenation products of glycerol.

5.1 Acceptorless dehydrogenation of glycerol



Scheme 13. Iridium catalysed dehydrogenation of glycerol to dihydroxyacetone.

Seminal work on the production of acceptorless dehydrogenation of glycerol was reported by Cole-Hamilton in 1988 using rhodium $[Rh(bipy)_2]Cl$ (bipy = 2,2′-bipyridine) and ruthenium $[RuH_2(N_2)(PPh_3)_3]$ catalysts.[187] However, details of the products obtained from the dehydrogenation reaction were not reported. Farnetti reported the synthesis of dihydroxyacetone (DHA) from

the dehydrogenation of glycerol with a TON of 2-11.[188] The reaction was catalysed by organoiridium complexes of the type [HIr(cod)L] (**Ir-7**, cod = 1,5-cyclooctadiene; L = Pr^n-$N(CH_2CH_2PPh_2)_2$, $Et_2NCH_2CH_2N(CH_2CH_2PPh_2)_2$, *o*-$Me_2NC_6H_4PPh_2$). Both acceptorless dehydrogenation and dehydrogenation in the presence of a hydrogen acceptor were demonstrated (Scheme 13).

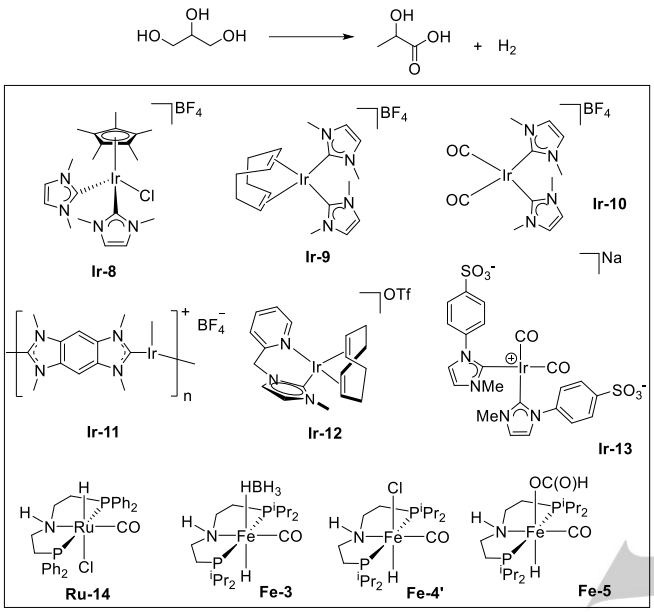
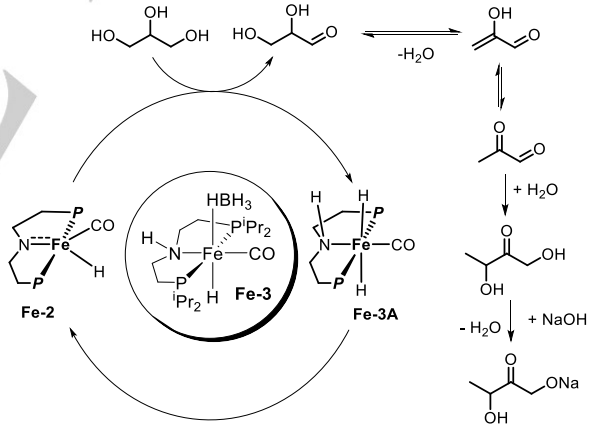


Figure 11. Homogeneous catalysts for dehydrogenation of glycerol to lactic acid.

Examples of the conversion of glycerol to lactic acid have been reported using hydrogenolysis under basic conditions in the presence of heterogeneous catalysts.[189–193] However, these processes suffer from the drawbacks of harsh reaction conditions (temperature ~200 °C) and lower chemoselectivity. Recently, Campos and Crabtree have reported the first example of acceptorless dehydrogenation of glycerol to lactic acid.[194] Several cationic iridium complexes (0.007 mol%) were screened for the dehydrogenation of glycerol under basic conditions of 8 M KOH (0.6 equiv. with respect to glycerol) at 115° C for 15 h. A TON of 1150 (**Ir-8**, Figure 11) and 2400 (**Ir-9**, Figure 11) were obtained. Remarkably, with **Ir-10** (Figure 11), a TON of 30,100 was obtained using only 20 ppm of catalytic loading. Furthermore, the selectivity of lactic acid was also found to be excellent (up to 97%) with propanediol, ethylene glycol, and formic acid being the main side products. In this direction, Tu, in 2015 reported dehydrogenation of glycerol to LA using a coordination polymer of iridium (**Ir-11**, Figure 11) as a catalyst with a TON of up to 1.24×10^5 even in a large-scale reaction under neat conditions.[195] Around the same time, Beller reported dehydrogenation of glycerol to lactic acid using ruthenium pincer catalysts.[196] The best results were obtained using Ru-Macho catalyst **Ru-14** (Figure 11) at 140 °C in N-methylpyrrolidine solvent under basic condition (NaOH) exhibiting TONs of up to 265,000 and a moderate selectivity of LA (67%). Soon after, Williams in 2016 reported a highly active iridium catalyst **Ir-12** (Figure 11) for the dehydrogenation of glycerol to LA under basic conditions exhibiting the highest TON of 4.56×10^6 for this transformation.[197] Remarkably, dehydrogenation of crude glycerol obtained directly from a biodiesel refinery was also demonstrated using the catalyst **Ir-12** with high selectivity of up to 99%. Recently, Voutchkova-Kosta has reported a series of water-soluble iridium catalysts for the conversion of glycerol to LA under basic conditions.[198] The iridium complex $[(NHC\text{-}ph\text{-}SO_3^-)_2Ir(CO)_2]^-$ (**Ir-13**, Figure 11), was found to be the most active catalyst exhibiting a TOF of 45, 592 h^{-1} under microwave conditions and performed 2,93,249 turnovers in 8 hours.

In addition to the precious metals, one example of the base-metal catalyst for the dehydrogenation of glycerol to LA has also been reported by Crabtree and Hazari in 2015.[199] Several iron PNP pincer catalysts (0.02 mol%) were screened under basic conditions (NaOH) at 140 °C for 3 h revealing pincer borohydride and formate complexes **Fe-3** and **Fe-5** (Figure 11) to be the most active catalysts exhibiting TON of up to 1050. A mechanism involving an amide complex **Fe-2** and a dihydride complex **Fe-3A** was proposed as outlined in Scheme 14. Complex **Fe-2** can be formed from **Fe-4'** by amine-deprotonation and the concomitant loss of chloride. Complex **Fe-3A** can be formed by base-assisted loss of BH_3 from **Fe-3** or a Lewis acid assisted decarboxylation of **Fe-5**. The amide complex **Fe-2** dehydrogenates glycerol to form glyceraldehyde and the dihydride complex **Fe-3A**. Glyceraldehyde is converted to lactic acid through a series of base-catalysed reactions – dehydration, tautomerization, and intramolecular Cannizaro reaction as shown in Scheme 14. Lactic acid is trapped as a corresponding salt in the presence of a base and the dihydride complex **Fe-3A** releases H_2 via metal-ligand cooperation to regenerate complex **Fe-2**.



Scheme 14. Proposed mechanism for the dehydrogenation of glycerol to lactic acid (*P* = P^iPr_2).

5.2 Glycerol as a hydrogen source for the transfer hydrogenation reactions

An important research topic in the area of catalytic transfer hydrogenation (TH) is to find a renewable, abundant, and non-toxic chemical that can act as a hydrogen source. Glycerol with the current market stage of overproduction fits well in these criteria. Moreover, it has a number of advantages to be used as a solvent. For example, (a) it has a high solubility of inorganic salts, acids, and bases, and (b) because of its high boiling point, reactions can be carried at high temperatures, and products can be easily distilled out from the reaction. A few examples have been reported for using glycerol in TH reactions using

homogeneous catalysts (Figure 12). The first example was reported by Crotti in 2009 using organoiridium complexes of the type Ir(diene)(N-N)X (diene = 1,5-hexadiene,1,5- cyclooctadiene; N-N = 2,2'-bipyridine, 1,10-phenanthroline and substituted derivatives; X = Cl, I) under basic conditions.[200]

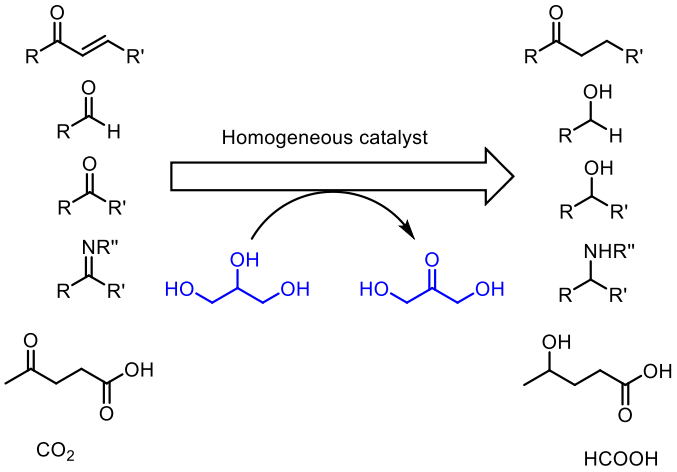


Figure 12. Transfer hydrogenation of organic compounds using glycerol as a hydrogen source.

Acetophenone was hydrogenated to phenyl ethanol at 100 °C using glycerol as a hydrogen donor source, where glycerol was transformed into dihydroxyacetone. In the same year, Tavor reported transfer hydrogenation of aldehydes and ketones using glycerol in the presence of [Ru(p-cumene)Cl_2]-dimer as a catalyst.[200] Along this direction, Farnetti in 2010 reported transfer hydrogenation of acetophenone, cyclohexanone, styrene, and aldehyde using glycerol in the presence of organoiridium catalysts. In 2011, Mata and Peris reported transfer hydrogenation of aldehydes and ketones using glycerol as a hydrogen donor and solvent.[201] Remarkably, the selective reduction of olefinic double bonds was observed for α,β-unsaturated ketones. The reaction was catalysed by Ir(III) complexes **Ir-14** and **Ir-15** (Figure 13) featuring electron-rich chelating bis-NHC ligand and tethered sulfonate group that enhances the solubility of catalyst in glycerol. Soon after that in 2012, Mata and Colacino reported more active iridium NHC catalysts **Ir-16** and **Ir-17** (Figure 13) for the transfer hydrogenation of aldehydes and ketones using glycerol.[202] Dihydroxyacetone was observed as the main dehydrogenation product of glycerol. In 2017, Voutchkova-Kosta reported a series of ruthenium(II) and iridium(III) N-heterocyclic carbene (NHC) complexes functionalized with sulfonates for the transfer hydrogenation of aldehydes, ketones, and imines using glycerol.[203] Catalyst **Ru-15** (Figure 13) was found to be the most active for the TH of ketones whereas catalyst **Ir-18** (Figure 13) was found to be the most active for the TH of imines and aldehydes.

In addition to the TH of aldehydes, ketones, imines, and olefins, glycerol has also been utilized for the TH of levulinic acid which can be derived from biomass. Recently, Voutchkova-Kosta reported highly active catalysts based on iridium N-heterocyclic carbene (NHC) complex for the TH of levulinic acid to Y-hydroxyvaleric acid (GHV)using glycerol as a hydrogen donor under basic conditions (KOH) at 150 °C.[204] A quantitative yield of GHV was obtained using just 1 ppm of catalyst **Ir-13** (Figure 11) exhibiting a TON of 101,100 and TOF of 50,550 h^{-1}. Glycerol was dehydrogenated to form lactic acid.

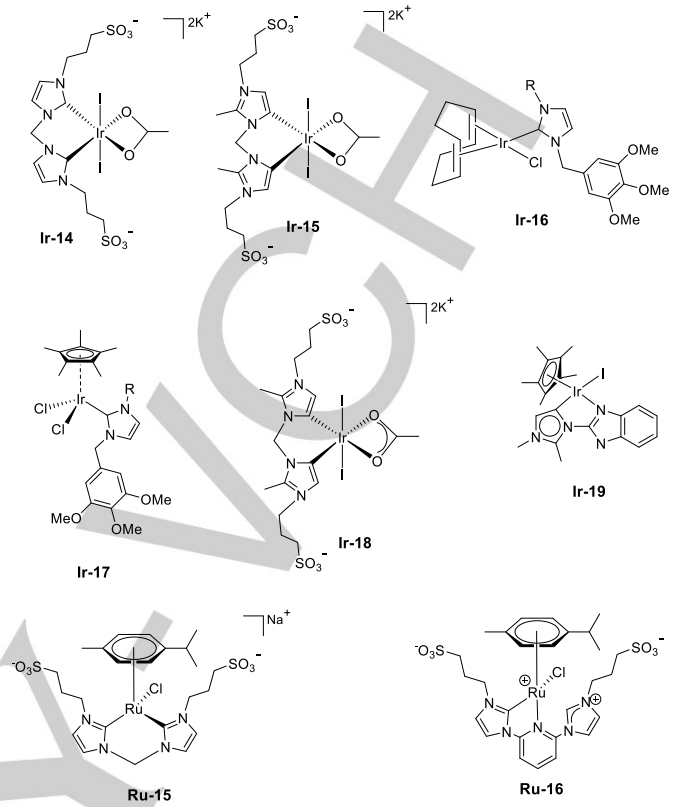


Figure 13. Homogeneous catalysts for transfer hydrogenation using glycerol as hydrogen source.

Along the direction of utilizing glycerol as hydrogen donors for the TH reactions, Voutchkova-Kosta reported TH of CO_2 to formate under basic conditions catalysed by a water-soluble ruthenium-NHC complex (**Ru-16**, Figure 13).[205] The catalytic activity was found to be dependent on the pH as under low pH conditions the reverse reaction i.e. dehydrogenation of HCOOH to CO_2 was also operative. A higher pH was achieved by reducing CO_2 pressure as the solubility of KOH would increase on decreasing CO_2 concentration. Indeed, reducing CO_2 pressure from 48 bar to 26 bar almost doubled the catalytic activity. Similarly, the catalysis was found to be dependent on temperature as at a higher temperature thermal decomposition of potassium formate was more favorable. Thus, the best activity was obtained by optimizing both the temperature and the base concentration. At 150 °C, CO_2 (26 bar) was hydrogenated in the presence of **Ru-16** (Figure 13), KOH (2 M), and glycerol (6.85 M) to produce an equimolar amount of lactate and formate (~600 turnovers). Additionally, carbonate salts such as K_2CO_3 can also be hydrogenated under the same conditions to form the same products with an even higher rate exhibiting TONs of 42,610 (lactate), 3,588 (formate), and 5,649 (1,2-propanediol). Recently, Choudhury has also reported TH of CO_2 to formate using an iridium catalyst of the type [Cp*Ir(NHC−benzimidazolato)] (**Ir-19**, Figure 13).[206] Compared to the system reported by Voutchkova-Kosta that operates at 26 bar CO_2 and gives TOF of 44 h^{-1} (24 h), Choudhury's system can work under 1 bar CO_2 pressure exhibiting a higher TOF of 90 h^{-1} (12 h) at 150 °C. Very recently, Jung and Jang have developed a superior catalyst for the TH of inorganic carbonates (K_2CO_3, $KHCO_3$, Na_2CO_3, $NaHCO_3$) using

glycerol to form formates and lactates exhibiting higher TONs and TOFs for formates (TON 16,856 and TOF 843 h^{-1}) and for lactates (TON 32,609 and TOF 1630 h^{-1}). The reaction is catalysed by Ir(bis-carbene) complexes where catalytic activity was found to be strongly dependent on the structural properties of biscarbene ligands, such as the length of the alkyl chain between two carbene moieties.[207]

6. Summary and Outlook

Processes based on catalytic (de)hydrogenation present attractive opportunities to transform chemical waste products into valuable resources or feedstocks enabling a circular economy. However, a central challenge remains on the production route of hydrogen gas. Most of the hydrogen gas is currently produced from fossil fuels that emit CO_2 in the atmosphere. Thus, in order to utilize (de)hydrogenation technologies for circular economy and sustainable reactions, it is crucial to develop parallel economic and efficient green technologies for the production of hydrogen gas such as water electrolysis using renewable energy or production of hydrogen gas from biomass.

Although it cannot be claimed that conversion of CO_2 to useful feedstock can solve the burning issues of climate change, but it would certainly allow us to be less dependent on fossil fuels and cut the carbon emission to a significant extent. Plenty of research has been developed which consumes CO_2 using hydrogenation pathways to make several highly useful chemical feedstocks such as formic acid and methanol. Due to unfavorable thermodynamics, direct hydrogenation of CO_2 to HCOOH under neutral conditions is challenging, and therefore most of the active catalytic systems are based on using a stoichiometric amount of a base posing an economic and sustainability hindrance in front of commercialization of this process. In the case of methanol, a few catalysts, although heterogeneous ones have been demonstrated at the pilot plant scale for the hydrogenation of waste CO_2 to methanol. The “greenest” renewable methanol in the world is produced by Carbon Recycling International (CRI) using hydrogenation of CO_2 where H_2 is produced from a renewable source. Utilizing Emission to Liquid technology, the plant has the annual capacity of producing 50,000-100,000 tons of methanol.[208]

Whereas substantial efforts have been dedicated towards CO_2 reduction, the area of N_2O reduction has received scant attention. Only one example has been reported for the direct hydrogenation of N_2O using a homogeneous catalyst (Scheme 6). A new and challenging direction in the area of N_2O reduction could be direct hydrogenation of N_2O to NH_3 or N_2H_4 using molecular hydrogen.

The crisis of plastic pollution is one of the biggest growing concerns of recent times, and in the past decade, several processes have been demonstrated for the closed-loop recycling of plastics. Methods based on catalytic (de)hydrogenation using molecular complexes have also been explored for both production and degradation of plastics although only at the proof of concept level as discussed above. More efforts need to be diverted towards developing active, inexpensive, and recyclable catalysts that could lead to the commercialization of such processes.

Likewise, although dehydrogenation of waste glycerol for the production of dihydroxyacetone and lactic acid have been reported, there are several scopes of development of efficient catalyst and new dehydrogenative coupling reactions involving glycerol such as dehydrogenative coupling of glycerol to make useful plastic such as polyesters, polyamides, and polycarbonates. Moreover, glycerol which is a renewable hydrogen-rich liquid has not yet been demonstrated for a Liquid Organic Hydrogen Carrier. New ligand design could facilitate the discovery of new (de)hydrogenation catalysis involving glycerol.

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Keywords: Homogeneous Catalysis • Hydrogenation • Dehydrogenation • Circular Chemistry • Green Chemistry

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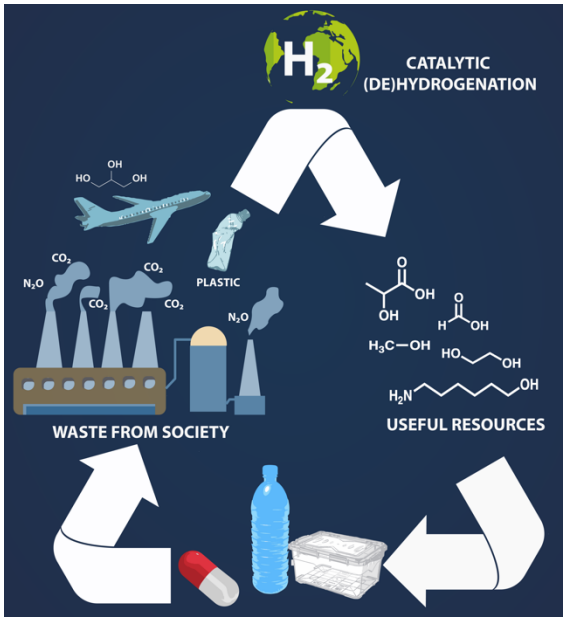

Our current dependence on rapidly depleting resources and the growing accumulation of chemical waste have become a grave concern to our society. This has sparked interest in the contemporary catalysis community to develop green technologies for the chemical conversion of waste products to valuable feedstocks enabling the circular economy. This article reviews the applications of homogeneous (de)hydrogenative catalysis for the conversion of chemical waste products – CO_2, N_2O, plastics, and glycerol to useful chemical feedstocks.